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CCCLII.—*The Two* o-*Cyanocinnamic Acids.*

By WILLIAM DAVIES and HARRY GORDON POOLE.

ALTHOUGH the two theoretically possible stereoisomeric forms of *o*-cyanocinnamic acid exist, only one form of *o*-carboxycinnamic acid is known, and this is obtained when either of the cyano-acids is hydrolysed (Edwards, J., 1926, 816). It gives the lactone of β-*o*-carboxyphenylhydracrylic acid on heating or on treatment with dehydrating agents, and attempts to prepare the true anhydride failed.

The *o*-cyanocinnamic acid melting at 256° can be obtained in 36% yield by heating the sodium salt of 1-nitroso-2-naphthol with a solvent of suitable boiling point, whereas with the use of sand as diluent (D.R.-P. 116,123) the yield is not more than 5% (Gabriel, *Ber.*, 1916, **49**, 1611). The *o*-cyanocinnamic acid melting at 137° has been prepared after D.R.-P. 411,955 by the action of *p*-toluenesulphonyl chloride on 1-nitroso-2-naphthol in the presence of aqueous alkali. During a large-scale preparation in which the heating during evaporation was very prolonged, an appreciable quantity of acetophenone-*o*-carboxylic acid was produced, possibly owing to the following changes in the $CH{\cdot}CH{\cdot}CO_2H$ group of the carboxycinnamic acid formed by hydrolysis of the cyanocinnamic acid initially produced: $\cdot CH{:}CH\cdot CO_2H \longrightarrow \cdot C(OH){:}CH\cdot CO_2H \longrightarrow \cdot CO\cdot CH_2\cdot CO_2H \longrightarrow \cdot CO\cdot CH_3$. It is, however, not clear whether the atmosphere or part of the nitrosonaphthol is the oxidising agent, and this abnormal reaction will be further examined.

EXPERIMENTAL.

The Preparation of o-*Cyanocinnamic Acid* (m. p. 256°).—A series of experiments was carried out with *p*-cymene, *o*-nitrotoluene, and nitrobenzene as solvents and the following process was found satisfactory. The dry, finely powdered sodium salt of 1-nitroso-2-naphthol (20 g.) and nitrobenzene (120 c.c.) were heated at 205° for 2 hours. The dark mixture was shaken with a warm aqueous solution of sodium acetate, and the aqueous portion was boiled with animal charcoal and acidified with hydrochloric acid; the buff-coloured precipitate obtained (yield, 6½ g. or 36%) crystallised from nitrobenzene in colourless needles, m. p. 256° (decomp.).

This *o*-cyanocinnamic acid sublimes almost unchanged at 225°/1 mm. It is not attacked by cold concentrated sulphuric acid exposed to air, and no trace of an acid amide is formed on prolonged standing. Hydrolysis with concentrated aqueous alkaline solutions gives a large quantity of tar and only a small amount of

o-carboxycinnamic acid (m. p. 184°). The identity of this carboxycinnamic acid with that from *o*-cyanocinnamic acid (m. p. 137°) was proved by the method of mixed melting points.

Preparation of o-*Cyano*allo*cinnamic Acid* (m. p. 137°) *after* D.R.-P. 411,955.—To a solution of 1-nitroso-2-naphthol (from 50 g. of β-naphthol *) in aqueous sodium hydroxide [45 g. (3¼ mols.) in 1 l.] at 75°, *p*-toluenesulphonyl chloride (65 g.) was added all at once. The temperature was then rapidly raised to 100° and maintained for 15 minutes; a vigorous reaction began at 85°. Some tar was filtered off when cold, and after acidification a large, orange-yellow precipitate settled out. When this was crystallised from hot water, 15 g. of cyanocinnamic acid (m. p. 137°) were obtained, and subsequently 6 g. of a yellow, granular material.

Acetophenone-o-carboxylic Acid.—In a preliminary experiment (1-nitroso-2-naphthol from 200 g. of β-naphthol; 10 l. of water; 3¼ mols. of sodium hydroxide; 320 g. of *p*-toluenesulphonyl chloride) the procedure was as described above. After the 15 minutes' heating at 100°, the mixture was rapidly cooled to 40° with ice. A large amount of a green substance like the sodium salt of nitrosonaphthol was left. The filtrate from this was evaporated to 4½ litres, and the green substance (assumed to be the sodium salt of nitrosonaphthol) then added together with the requisite amounts of sodium hydroxide and toluenesulphonyl chloride. The mixture was kept at 100° for 15 minutes, and on cooling, a green precipitate was again formed. The filtrate when acidified with hydrochloric acid gave much tar, and after the removal of this the solution was again made alkaline with sodium hydroxide solution; a dark substance slowly separated from the deep red solution. This solution was concentrated and acidified with hydrochloric acid, whereby, instead of *o*-carboxycinnamic acid, a deep red oil was produced. This was extracted with ether, the ether removed, and the pasty residue crystallised from water, 20 g. of crude crystalline acetophenone-*o*-carboxylic acid being obtained. This crystallised from benzene in colourless prisms, which melted at 114—115° and had a sweet taste (Found: equiv., 165·4; *M*, by Rast's method, 163, 171; H, 5·2. Calc. for $C_9H_8O_3$: equiv. and *M*, 164; H, 4·9%) (compare Gabriel and Michael, *Ber.*, 1877, **10**, 1554. Rule and Smith, J., 1926, 556, record m. p. 112°). The *oxime* crystallised from alcohol in colourless needles, m. p. 156—157°, and the p-*nitrophenylhydrazone* in minute, yellow, felted needles, m. p. 211°. The *phenylhydrazone*

* β-Naphthol is nitrosated in about 85% yield after Lagodzinski and Hardine (*Ber.*, 1894, **27**, 3075), and is most conveniently used moist. The nitrosonaphthol is difficult to dry completely, and the sodium salt when dry is very sternutatory.

is too soluble in water to be a convenient derivative for identification. The acid was smoothly converted into phthalic acid by oxidation with permanganate solution.

Properties and Derivatives of o-*Cyano*allo*cinnamic Acid.*—On being heated slightly above its melting point under 1 mm. pressure, this acid distils with some decomposition. The oily distillate, which has the odour of styrene, contains the isomeric *o*-cyanocinnamic acid, m. p. 256°. The *allo*-acid is easily hydrolysed to the corresponding dicarboxylic acid (m. p. 184°).

o-*Cyano*allo*cinnamyl chloride* is best prepared by heating the corresponding acid with a slight excess of thionyl chloride for 1 hour; the excess of thionyl chloride is then removed in a vacuum. The residual acid chloride crystallises from petroleum (b. p. 120°) in colourless needles, 2 cm. long (Found: Cl, 18·4. $C_{10}H_6ONCl$ requires Cl, 18·5%). It melts at 50°, and is extremely soluble in benzene, ether, or dichloroethylene, and sparingly soluble in cold light petroleum. Ethyl and methyl alcohol convert it into the ethyl and methyl esters of the lactone of β-*o*-carboxyphenylhydracrylic acid (Roth, *Ber.*, 1914, **47**, 1598), m. p. 76° and 62°, respectively.

The authors wish to thank Mr. F. C. Woods, M.Sc., for assistance in preparing the *o*-cyanocinnamic acid of m. p. 256°.

MELBOURNE UNIVERSITY, AUSTRALIA. [*Received, April 20th*, 1927.]

CCCLIII.—*Beryllium Dialkyls.*

By HENRY GILMAN and F. SCHULZE.

IN continuation of studies on organoberyllium halides (Gilman, *J. Amer. Chem. Soc.*, 1925, **45**, 2693; see also Durand, *Compt. rend.*, 1926, **182**, 1162) it was necessary to prepare some beryllium dialkyls for comparative purposes, inasmuch as the two classes of compounds appear to be interconvertible.

Cahours (*Ann. Chim. Phys.*, 1860, **58**, 22) claimed to have prepared beryllium diethyl by heating the metal with ethyl iodide in a sealed tube. Later (*Compt. rend.*, 1873, **76**, 1383. Cahours's work on beryllium dialkyls has been discussed by Frankland, J., 1861, **13**, 181, 194) he reported the preparation of beryllium diethyl and beryllium dipropyl by heating the metal with the corresponding mercury dialkyls in a sealed tube at 130°. It is highly probable that Cahours's work on beryllium diethyl is incorrect. His beryllium diethyl was distilled in an atmosphere of carbon dioxide and boiled

at 185—188°. We have found that beryllium diethyl not only reacts with carbon dioxide, but also boils at a much higher temperature range (with decomposition) than that reported by Cahours. Furthermore, we had no success in the preparation of beryllium diethyl and beryllium di-*n*-butyl from the mercury dialkyls as recommended by Cahours. Incidentally, Cahours incorrectly described magnesium diethyl as a liquid, inasmuch as it is a solid (Gilman and Schulze, *J. Amer. Chem. Soc.*, 1927, **49**, 2328).

Lavroff (*J. Russ. Phys. Chem. Soc.*, 1884, **16**, 93; *Bull. Soc. chim.*, 1884, **41**, 548) very briefly mentioned the preparation of beryllium dimethyl by the action of beryllium on mercury dimethyl in a sealed tube at 130°. We have found no further mention of his work. Despite the very meagre detail in his preliminary communication, it is quite probable that he did have beryllium dimethyl.

Krause and Wendt (*Ber.*, 1923, **56**, 467, footnote 2) state that beryllium dialkyls may be prepared by the reaction between beryllium chloride and an excess of Grignard reagent.

Experimental.

Several unsuccessful attempts were made to prepare beryllium diethyl and beryllium di-*n*-butyl from finely crushed beryllium and equivalent quantities of the corresponding mercury dialkyls. No evidence of reaction was obtained when the mixtures were kept in sealed tubes for 3 weeks at room temperature; when they were heated for 3 weeks at 90°, some free mercury was formed, and heating for 15 hours at 130°, 175°, 200°, and 225° apparently induced only decomposition of the mercury dialkyls; in no case was there evidence of the formation of beryllium dialkyls.

Beryllium diphenyl and beryllium di-*p*-tolyl may be readily prepared by heating beryllium with equivalent quantities of mercury diphenyl and mercury di-*p*-tolyl and a trace of mercuric chloride in sealed tubes at 225° for 6 hours.

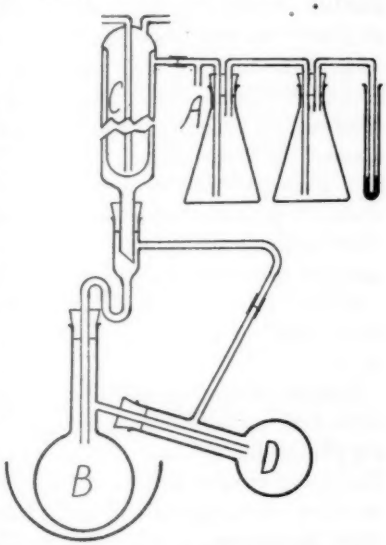
In the experiments with mercury dialkyls, no mercuric chloride was added. Other studies (Gilman and Schulze, *loc. cit.*) have shown that mercuric chloride is an almost indispensable catalyst in the preparation of some metallic dialkyls, like magnesium diethyl. No attempt was made to prepare beryllium dimethyl from beryllium and mercury dimethyl. It is quite reasonable to assume that traces of some mercuric halide were contained in the materials used by Lavroff. The beryllium used in the present studies was obtained from the Beryllium Corporation of America and contained more than 99·5% of beryllium.

It is possible to prepare beryllium dialkyls by heating beryllium with the appropriate alkyl halides, an alkylberyllium halide being

an intermediate product. Here, again, mercuric chloride is a very helpful catalyst.

However, it appears that the most convenient method for the preparation of beryllium dialkyls is the reaction between anhydrous beryllium chloride and the appropriate Grignard reagent. We have prepared beryllium dimethyl, diethyl, and di-*n*-butyl by this method.

Preparation of Beryllium Dialkyls.—Because of the highly hygroscopic nature of anhydrous beryllium chloride and the ready decomposability of beryllium alkyls and the Grignard reagent by air, all operations were carried out in pure dry hydrogen or nitrogen, admitted through the tube *A*. Anhydrous beryllium chloride (8 g.; 0·1 g.-mol.) is dissolved in 50 c.c. of anhydrous ether, cooled by running water. The filtered oily solution, which may be either colourless or pale yellow and separates into a lower layer of beryllium chloride etherate and an upper layer consisting largely of ether, falls directly into 75 c.c. of 4*M*-magnesium methyl iodide (0·3 g.-mol.) contained in a 250 c.c. flask, *B*, the Grignard solution being gently shaken during addition. There is little heat of reaction if the beryllium chloride solution is pure and anhydrous. The formation of white clouds on the surface of the reaction mixture is indicative of the presence of air or oxygen.



The excess of ether is removed by stopping the circulation of water in the condenser, *C*, until the oil-bath attains a temperature of 150°. The water is then turned on slowly in order to prevent a too sudden contraction (due to the condensation of ether) that might draw air into the condenser and receiving flask. Distillation is continued at 150—200° for 6 to 15 hours, so long as an ethereal solution of beryllium dimethyl collects in the receiving flask, *D*. Heat radiating from the oil-bath is sufficient to keep the temperature of the receiver above the boiling point of ether and thereby prevent the condensation of more ether than is necessary to hold the beryllium dimethyl in solution. The distillation may be continued overnight, as it requires no attention. Should the ether be driven out

completely from the distilling flask, *B*, so that no more ether vapour circulates, it is necessary merely to heat the receiver gently to return the ether to flask *B*. Such heating should be moderate, otherwise some of the beryllium dimethyl will be driven back into *B* and so extend the time of recovery of the compound.

The ethereal solution of beryllium dimethyl obtained in this manner is clear and colourless (when care has been taken to exclude air), and it may be used directly in a study of the reactions of the compound. When not in use, it is kept preferably in sealed glass containers. Pure, ether-free beryllium dimethyl is obtained by heating the distillate. At about 100—125°, most of the ether is expelled and the whole solution suddenly turns to a mass of white needles containing some ether, which may be removed by heating to 200°. At 200° (external temperature), the compound commences to sublime rapidly, and part of it solidifies in the capillary when a constricted test-tube is used for the collection of ether-free samples. However, the capillary can be kept open prior to sealing by applying a small luminous flame. A repetition of this process of distillation in a sealed U-tube arrangement originally filled with ether vapour makes it possible to obtain material free from oxide or methoxide by alternately heating and cooling each part of the U-tube. The samples used for analysis were prepared in this manner.

3·5 G. (90% yield) of beryllium dimethyl were obtained from 0·1 g.-mol. of beryllium chloride; with 0·3 g.-mol., the yield was 84·7%.

Beryllium diethyl and di-*n*-butyl were prepared in essentially the same way as beryllium dimethyl. However, it is possible to distil beryllium diethyl and di-*n*-butyl directly in a vacuum. Because of the higher vapour pressure of beryllium di-*n*-butyl, it would probably be more advantageous to use a vacuum distillation rather than the ether distillation or ether sublimation process used for the dimethyl compound.

Analysis of Beryllium Dimethyl.—After being weighed, one of the sealed tubes, containing beryllium dimethyl prepared by distillation at 200°, was broken in a vessel filled with dry ether, and the volume of methane liberated on the addition of water and then dilute hydrochloric acid was measured in a special eudiometer containing concentrated sulphuric acid. An aliquot portion of the evolved gas, when exploded with a measured volume of oxygen, was shown to consist of pure methane.

The beryllium was analysed as beryllium oxide after careful removal of the glass, which was weighed to determine the weight of beryllium dimethyl originally present in the sealed container [0·1501 g. of beryllium dimethyl gave 173·2 c.c. (corr.) of methane

and 23·33% of beryllium. Calc.: 171·4 c.c. and 23·25%. 0·1771 G. gave 200·7 c.c. of methane. Calc.: 202·2 c.c.].

Properties of Beryllium Dialkyls.—Beryllium dimethyl crystallises from hot concentrated ethereal solution in snow-white needles (see Preparation). It is also deposited in the same form when it sublimes, without melting, at about 200°. The method of preparation is based on its high volatility in ether, and these ethereal solutions fume strongly when exposed to the atmosphere. When suddenly overheated, it undergoes partial decomposition, leaving a brown or grey mirror.

Beryllium diethyl is a colourless liquid, b. p. 93—95°/4 mm. and 110°/15 mm. It distils between 180° and 240° at atmospheric pressure with considerable decomposition. The compound is only distilled with difficulty because of its pronounced tendency to become superheated and then break suddenly into foam. This may be due to the decomposition of an etherate. A part of the purest material solidified, in a carbon dioxide–ether freezing mixture, to white crystals which on warming melted at −13° to −11°.

Beryllium di-*n*-butyl is a clear, colourless liquid having a mercaptan-like odour. The boiling point, 170°/25 mm., was determined with a rather small quantity of material and so may not be taken with too much credence.

Both beryllium dimethyl and diethyl are spontaneously inflammable in the air, and especially so in a humid atmosphere. Even concentrated ethereal solutions are inflammable spontaneously in the presence of moist air. The compounds burn with luminous flames, evolving dense white fumes of beryllium oxide. Their very high sensitivity to oxygen made it difficult, at first, to purify the hydrogen or nitrogen to such an extent that it would not give a white cloud of beryllium oxide when passed over the ethereal solutions of the dialkyls. For this reason, a magnesium phenyl bromide solution was inserted in the drying and purifying train in order to remove a residuum of oxygen. Beryllium di-*n*-butyl is not spontaneously inflammable when exposed to the air. But it does oxidise rapidly, when so exposed, with the evolution of heat. Very probably, beryllium butyloxide is a product of such oxidation, inasmuch as the odour of *n*-butyl alcohol becomes quite pronounced after a short air exposure.

The reaction of the dialkyls with water is violent, and in the presence of small amounts of water the materials frequently inflame. Methane and ethane are evolved when the corresponding dialkyls are decomposed by water.

Beryllium dimethyl in the solid state inflames when treated with carbon dioxide. With an ethereal solution, however, the reaction

is quite mild and acetic acid is formed. An ethereal solution of beryllium diethyl reacts with carbon dioxide to give triethylcarbinol.

Phenylcarbimide in ethereal solution reacts with extreme violence with the three dialkyls studied. In each case, a white solid separated at first, and then dissolved in the excess of beryllium dialkyl. The expected anilides were obtained, the valeranilide as an oil. This anilide is known to crystallise with difficulty, so that its identity has not been confirmed, as was done with the other two anilides, by a mixed-melting point determination with an authentic specimen. Aceto-α-naphthalide was obtained from beryllium dimethyl and α-naphthylcarbimide.

The three dialkyls give an immediate positive colour reaction with Michler's ketone according to the test described by Gilman and Schulze (*J. Amer. Chem. Soc.*, 1925, **47**, 2002) for RMgX and some other organometallic compounds. The blue instead of green colour given by beryllium di-*n*-butyl indicates that this dialkyl probably reduced the ketone to Michler's hydrol (*loc. cit.*).

Beryllium dimethyl with benzophenone gave diphenylmethylcarbinol, which was identified as αα-diphenylethylene. Beryllium diethyl, on the other hand, reduced benzophenone to benzhydrol. In the latter reaction, a bright orange-red colour was present transitorily at the junction of the two liquids. This may be indicative of the intermediate formation of a free radical.

Beryllium dimethyl with benzoyl chloride gave phenyldimethylcarbinol, and this was identified by the formation of *iso*propenylbenzene when the carbinol was distilled. The reaction product was probably free from acetophenone as indicated by a test with semicarbazide.

The beryllium dialkyls appear to have high solvent characteristics, for all the intermediate reaction products dissolved in an excess of the dialkyl. Equally striking is the fact that beryllium diethyl dissolved the beryllium oxide and ethoxide formed by partial decomposition of the dialkyl, as well as the brown or grey mirror formed by the high-temperature decomposition of the dialkyl.

Beryllium dimethyl and diethyl react vigorously with iodine. When 1·343 g. of beryllium dimethyl were treated with 1 equiv. (4·353 g.) of iodine, the solution still contained some dialkyl, as was evidenced by the fuming on air exposure and by a slight positive test (Gilman and Schulze, *loc. cit.*). After standing for several days in a cork-stoppered flask, the solution no longer fumed and gave a negative test. Very probably beryllium methyl iodide was formed as a result of the iodine reaction, because the solution gave acetanilide on treatment with phenylcarbimide, and when heated it fumed and gave a positive test. These are among the criteria

included for the characterisation of beryllium alkyl halides (Gilman and Schulze, *J. Amer. Chem. Soc.*, 1927, **49**, Nov.).

Beryllium diethyl reacts with an excess of an ethereal solution of beryllium chloride to give a solution with the characteristics of beryllium ethyl chloride. In view of these latter experiments, the following equilibrium is probable under certain conditions:

$$BeR_2 + BeX_2 \rightleftharpoons 2RBeX.$$

In general, the beryllium alkyl halides are less active than the beryllium dialkyls, and the beryllium dialkyls are at least equal in activity to the Grignard reagents.

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[*Received, August 2nd*, 1927.]

CCCLIV.—*The Thermal Dissociation of Strontium Carbonate.*

By EDWARD OSWALD JONES and MAURICE LUND BECKER.

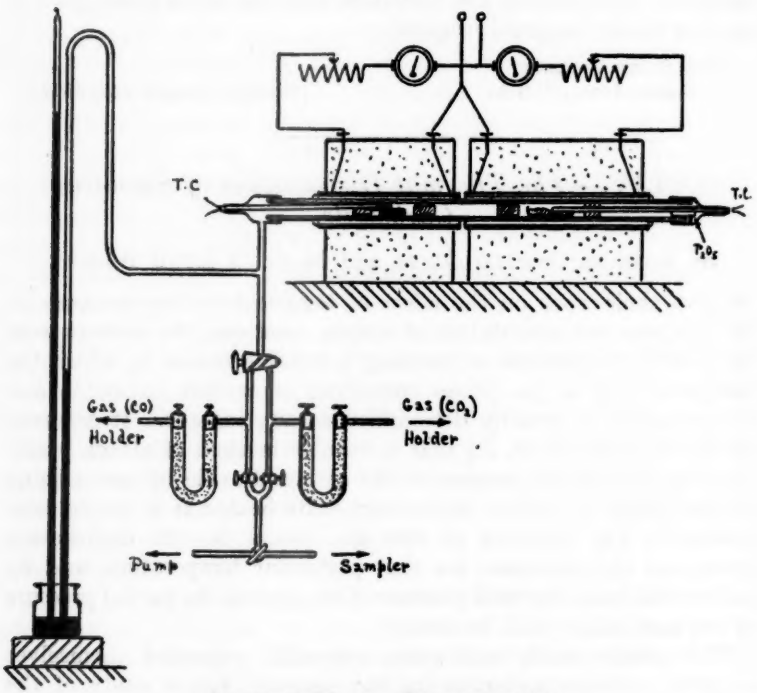
DURING their work on the effect of temperature and pressure on the progress and equilibrium of certain reactions, the authors were faced with the problem of devising a suitable means by which the composition of a gas phase consisting of carbon monoxide and dioxide could be readily determined at any instant. It occurred to one of them (E. O. J.) that a suitable method of attack would be to fix the partial pressure of the carbon dioxide by maintaining the gas phase in contact with a carbonate heated to a known temperature. The pressure of this gas would be the dissociation tension of the carbonate for that particular temperature, and by subtraction from the total pressure of the system the partial pressure of the monoxide could be found.

The alkaline-earth carbonates naturally suggested themselves as being suitable materials for the purpose, and a study of the literature led to the selection of strontium carbonate. The only work on the dissociation tension of this carbonate at different temperatures to which reference could be found was that of Pott (Diss., Freiburg, 1905; see also Mellor, "Treatise on Inorganic and Theoretical Chemistry," III, 655). Two other workers, Brill (*Z. anorg. Chem.*, 1905, **45**, 275) and Hedvall (*ibid.*, 1916, **98**, 47), record determinations of the temperature at which the tension attains 1 atm. Unfortunately, their work is not in good agreement with that of Pott, and it was further noted that Pott's curve is of quite a different shape from those given for calcium and barium carbonates, and actually cuts the first of these two curves. It

was thought advisable, therefore, to make a series of determinations of the dissociation tension of strontium carbonate at different temperatures in the same apparatus and under the same experimental conditions as those in which it was proposed to use this material for carbon dioxide-pressure control.

During the course of the investigations, two distinct types of apparatus were employed. These are diagrammatically represented in Figs. 1 and 2. The first was designed for use where it was neces-

FIG. 1.



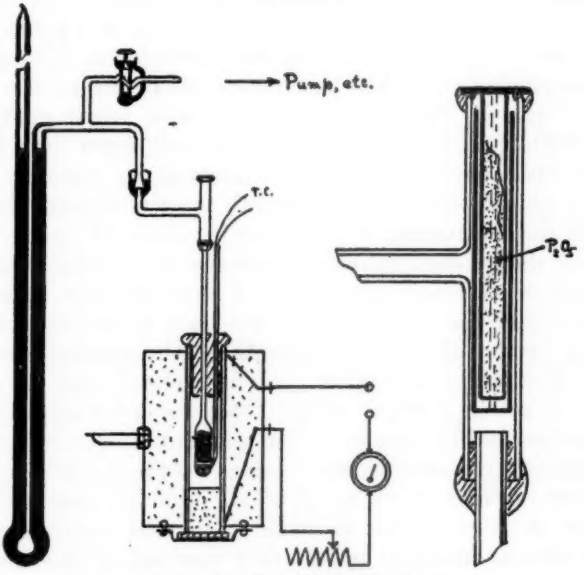
Apparatus No. 1. (Diagrammatic.)

sary to keep the carbonate separate from the other reactants with the gas phase, and where independent temperature control, both of the reactants and of the dissociating carbonate, was desirable. The second, which is simpler, was utilised when the above-mentioned limitations did not apply.

Apparatus 1 consists essentially of a long porcelain tube (800 mm. × 18 mm. internal diameter) heated by two independently controlled electric resistance furnaces. The ends of the tube were closed by glass caps hermetically sealed to the heating tube by white wax. Each of these caps had a small-bore extension to

take the thermocouple sheath, and one of them was also provided with a side tube which gave connexion to the manometer, evacuating pump, gas holders, etc. The Vitreosil thermocouple sheaths were sealed into the extension tubes of the caps by means of white wax, and it was also found advisable to close the open ends of these sheaths with wax, since, after being maintained at high temperatures for a considerable time, they developed slight porosity at the heated end, due to devitrification. Heat-insulating plugs, made of kieselguhr bonded with a small proportion of sodium silicate, were placed in the furnace tube to lessen heat radiation

FIG. 2.



Apparatus No. 2. (Diagrammatic.)

and to provide zones of uniform temperature. A boat containing phosphorus pentoxide, placed at one end of the tube, served to absorb all the water vapour.

Apparatus 2 is essentially a small, transparent silica bulb of about 10 c.c. capacity fused to a silica tube (30 mm. × 5 mm.), the other end of which is sealed by white wax into a glass T-piece. This serves to accommodate a small container for phosphorus pentoxide and to give connexion to the manometer, etc. A small resistance furnace, which may be raised or lowered, serves to heat the bulb to the required temperature, which is measured by a thermocouple in contact with the bulb wall.

This second form of apparatus is more suitable for measuring

dissociation tension, since equilibrium conditions are attained much more rapidly as a result of its small volume and its relatively larger carbonate content. Nevertheless, since it was necessary to use the first form of apparatus for some of the investigations, it was considered desirable to study the thermal dissociation of the carbonate in both forms of apparatus as a matter of precaution and for the sake of calibration. The results obtained were found to agree within the limits of experimental error, and this concordance is considered good presumptive evidence of the correctness of the values obtained.

The experimental details were essentially the same for each type of apparatus. A sufficient quantity of pure strontium carbonate (about 1 g. in the case of the bulb, and 4—5 g. in a porcelain boat in the case of the tube) having been introduced, the apparatus was hermetically sealed and then evacuated by means of a " Cenco Hyvac " pump. The temperature was now raised gradually to about 600°, during which time the evolved gases (largely water vapour) were removed at frequent intervals by pumping. When no more gas appeared to be given off, the temperature was raised to 1000° and maintained at this value for about 12 hours. During this time the pressure increased gradually, due probably to further expulsion of occluded gas and to a slow reaction between the carbonate and the silica walls of the bulb where contact occurs, whereby carbon dioxide was liberated. The apparatus was then evacuated rapidly, the tap to the pump closed, and the pressure allowed to attain a steady value. This was lower than the initial one obtained and the process was repeated as often as was necessary to obtain two consecutive equal values for the gas pressure. This procedure ensured (*a*) removal of all occluded gas, and (*b*) the presence of more strontium oxide than that equivalent to the carbon dioxide liberated by the slow reaction already mentioned. That this is so is shown by the fact that, on allowing the furnace to cool to 600°, the resulting vacuum was of a higher order than could be obtained by the pump alone, *i.e.*, less than 0·05 mm.

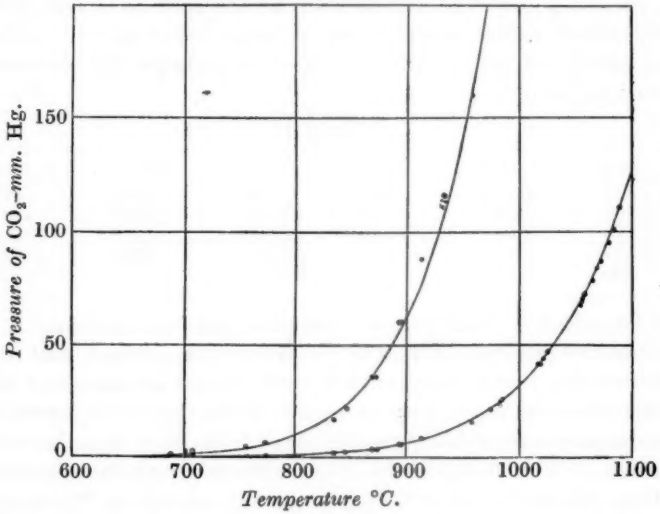
The apparatus was now ready for use. The strontium carbonate was slowly heated, and pressure and temperature readings were taken. In the case of the bulb apparatus, the rate of heating was sufficiently slow to ensure that the pressure corresponding to a given temperature was the equilibrium pressure until about 900° had been reached. Beyond this temperature, the furnace was allowed to reach a steady state before readings were taken. In the case of the tube furnace, the method of allowing the furnace to reach a steady temperature was practised from the beginning, as the gas evolution involved was so much larger.

The temperature was measured by means of carefully calibrated thermocouples and is considered accurate to within $\pm 3°$; pressures less than 10 mm. were read by means of a cathetometer to within $\pm 0{\cdot}05$ mm.; higher pressures were read directly on a metre scale fixed alongside the manometer. This gave readings to within $\pm 0{\cdot}5$ mm., which is as close as is justified by the accuracy of the temperature measurements.

Values of the dissociation tension for given temperatures were obtained on both ascending and descending temperature scales and

FIG. 3.

Dissociation of strontium carbonate.



further checked by haphazard alteration of the temperature; the concordance was good. In view of this agreement, there is no need to quote more than one set of results. Those obtained by one of the authors (M. L. B.) are recorded in Table I (in mm. Hg) and shown graphically in Fig. 3.

TABLE I.

Temp.	p, obs.	p, calc.	Temp.	p, obs.	p, calc.
689°	0·1	0·07	975°	21	21·5
708	0·3	0·12	984	25	24·5
756	0·5	0·35	1020	42	42
775	0·6	0·55	1027	47·5	47
835	1·7	1·85	1059	72·5	72
846	2·2	2·3	1070	84	84
869	3·6	3·5	1081	95	97
896	6·0	5·8	1090	111	110
913	8·8	7·8	1103	123	130
958	16·0	16·3			

The dissociation tensions of calcium and barium carbonates determined by various workers have been found to fit closely to curves of the form

$$\log p_1 - \log p_2 = -K(1/T_1 - 1/T_2)$$

where p_1 and p_2 are the pressures (mm. Hg), T_1 and T_2 the absolute temperatures, and K is a constant. It was of interest, therefore, to see whether the dissociation of strontium carbonate could be similarly expressed. If the value of the dissociation tension at 928° be taken as 10 mm. and K as $1{\cdot}05 \times 10^4$, then the values of the carbon dioxide pressure for other temperatures can be calculated. The resulting graph, as will be seen, agrees very satisfactorily with the observed values over the entire range investigated. Table II gives calculated values of the dissociation pressure for temperature increments of 50°.

TABLE II.

Temp.	p, mm.	Temp.	p, mm.	Temp.	p, mm.
650°	0·023	900°	6·19	1150°	231
700	0·090	950	14·36	1200	411
750	0·30	1000	31·22	1258	760
800	0·91	1050	63·98	1300	1167
850	2·47	1100	124·5		

It has already been pointed out that good concordance existed between the results obtained in the different apparatus, and further confirmation, particularly of the lower values as corrected to the calculated curve, is given by later work on the C–CO–CO_2 equilibrium where the carbon dioxide pressure is controlled by means of strontium carbonate. The values of the equilibrium constant thus determined for this system at different temperatures lie closely on Tigerschiöld's curve (*Jernkontoret's Annaler*, **1923**, 67; see also Johansson and von Seth, *J. Iron and Steel Inst.*, **1926**, **114**, 313) which correlates satisfactorily the work of Boudouard (*Ann. Chim. Phys.*, 1901, **24**, 5), Schenck (*Ber.*, 1905, **38**, 2139), and Rhead and Wheeler (J., 1910, **97**, 2178) on this equilibrium. This agreement justifies the acceptance of the results, and, in particular, the validity of the formula for calculating the dissociation tension in the lower temperature range.

The authors' value for the temperature at which the dissociation pressure is equal to 1 atm. is approximately 100° higher than those reported by Brill (*loc. cit.*) and Hedvall (*loc. cit.*). Although the authors' result has been obtained by extrapolation of the curve, whereas the others have experimental basis, it is regarded as more accurate for the following reasons. (*a*) Brill noted the temperature at which loss of weight just occurred from calcium carbonate in a

carbon dioxide atmosphere of approximately 760 mm. pressure, and obtained a value 75—100° lower than those recorded by other workers who measured the actual dissociation tension. This discrepancy for calcium carbonate is of the same order as the difference between Brill's result for strontium carbonate and the one put forward in this paper.

(*b*) Hedvall, who used the thermal arrest in the heating curve for fixing the dissociation temperature, gives 1141° as the temperature at which carbon dioxide evolution commences. It is of interest, however, that he quotes 1255° (only 3° different from the value put forward by the authors) as the temperature at which carbon dioxide evolution becomes rapid, and further states that a small quantity of strontium carbonate was not completely decomposed on being heated for 5 minutes at temperatures between 1141° and 1255°.

The authors' curve lies wholly between the accepted curves for calcium carbonate (Johnston, *Z. physikal. Chem.*, 1908, **62**, 330; *J. Amer. Chem. Soc.*, 1910, **32**, 938) and barium carbonate (Finkelstein, *Ber.*, 1906, **39**, 1585), thus differing from that of Pott. It is suggested that the higher values obtained by Pott in the lower temperature range are due to the absence of sufficient oxide phase to absorb the excess carbon dioxide liberated by some such slow carbonate–silica reaction as was noticed by the authors in their work. At higher temperatures, where the extent of dissociation involves the production of larger quantities of strontium oxide, this source of error tends to disappear, and it is of interest to note that Pott's results for 1256° and 1263° (744 mm. and 785 mm., respectively) would lie satisfactorily on the extrapolated portion of the authors' curve.

In view of the fact that Finkelstein (*loc. cit.*) obtained evidence of the formation of a basic barium carbonate ($BaO,BaCO_3$), the authors sought for indications of a similar basic strontium carbonate. When the dissociation tensions at 1000° and 1100° were being measured, a known volume (approximately one-sixth of the available carbon dioxide) was drawn off and the system allowed to return to equilibrium. The resulting pressure was the same as in the initial determination. This process was repeated until six withdrawals had been made. In every case, except the last, the pressure returned to the recorded equilibrium value, whilst on the last occasion the pressure only rose a few mm., showing that the solid phase was now wholly the oxide. This series of experiments shows that over the range 15—85 mols. % of strontium oxide the solid phase does not change in character, and therefore affords no evidence for the existence of a basic carbonate under these conditions.

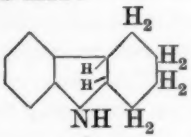
The work here described was carried out in the Metallurgical Department, Manchester University, and the authors desire to express their thanks to Prof. F. C. Thompson, D.Met., for the facilities provided and also for his interest and helpful criticisms and suggestions during the course of the work. Acknowledgment is also due to the Department of Scientific and Industrial Research and to the British Cast Iron Research Association for their financial grants and for their permission to publish the results.

THE UNIVERSITY, MANCHESTER. [*Received, September 7th*, 1927.]

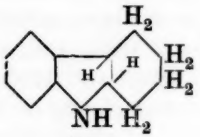
CCCLV.—*A New Stereoisomeride* (trans-) *of Hexahydrocarbazole.*

By JOHN GURNEY, WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT.

DURING the course of experiments on octahydroacridine, Perkin and Sedgwick (J., 1924, **125**, 2437) showed that this substance exists in two stereoisomeric, externally compensated modifications, namely (A), m. p. 82°, and (B), m. p. 72°, and these they subsequently resolved (J., 1926, 438) each into its optically active components. In the earlier paper, it was pointed out that hexahydrocarbazole also should exist in two analogous stereoisomeric forms, which may be represented thus:



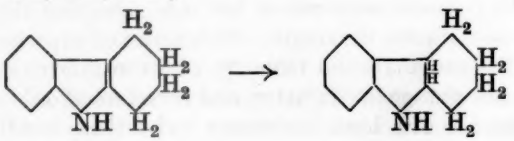
cis.



trans.

and it was proposed to investigate this point.

Hitherto only one form of hexahydrocarbazole (m. p. 99°) has been described. Although this substance has been obtained by the reduction of carbazole under various conditions (Graebe and Glaser, *Ber.*, 1872, **5**, 14; *Annalen*, 1872, **163**, 352; Schmidt and Sigwart, *Ber.*, 1912, **45**, 1784), the only practicable method for preparing relatively large quantities is by the hydrogenation of the double bond in tetrahydrocarbazole (Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 70; Carrasco, *Gazzetta*, 1908, **38**, ii, 303; Perkin and Plant, J., 1924, **125**, 1512).



By reducing a large quantity (900 g.) of tetrahydrocarbazole with tin and hydrochloric acid we have now succeeded in isolating a small amount (about 12 g.) of the second isomeride of hexahydrocarbazole, and we find that this melts at 127°. Its identity has been confirmed by making the *picrate* and *acetyl* and *benzoyl* derivatives, and comparing these with the corresponding derivatives of the ordinary form. Both modifications of hexahydrocarbazole have been shown to be unimolecular, they distil unchanged at the ordinary pressure at approximately the same temperature, and are both exceptionally volatile in steam.

The existence of two stereoisomerides of hexahydrocarbazole can be predicted from the Sachse–Mohr theory of multiplanar rings and forms an interesting addition to the cases of this kind which have been already described. This type of stereoisomerism has been recently well established by several investigators in the decahydronaphthalene series, and in a few other dicyclic systems composed of two six-membered rings (see, *e.g.*, Windaus, Hückel, and Reverey, *Ber.*, 1923, **56**, 91; Perkin and Sedgwick, *loc. cit.*; Helfer, *Helv. Chim. Acta*, 1926, **9**, 814; Hückel and Stepf, *Annalen*, 1927, **453**, 163). In all these cases, both the *cis*- and the *trans*-modifications can be regarded as strainless. The points of particular interest involved in the case of hexahydrocarbazole are (1) that the stereoisomerism is a feature of a dicyclic system composed of one six-membered carbon ring and one five-membered ring containing nitrogen, and (2) that both isomerides are produced together from the same substance in the same reaction. It is quite apparent that in this system there is far more strain in the *trans*-structure than in the *cis*-, a fact which is easily demonstrated with the aid of models. It is to be expected, therefore, that in the formation of such a dicyclic system by the hydrogenation of the double bond common to both rings the *cis*-modification will be produced to a much greater extent than the *trans*-modification, and this is exactly what is observed in the case of the hexahydrocarbazoles. There can be little doubt that the modification, m. p. 99°, which constitutes almost the entire product, is the *cis*-, and that the new substance, present to the extent of 1—2%, is the corresponding *trans*-form.

Hückel and Friedrich (*Annalen*, 1926, **451**, 132) have isolated the *cis*- and *trans*-modifications of the hexahydro-β-hydrindones and the three hexahydro-β-hydrindols, which contain dicyclic carbon systems composed of one six-membered and one five-membered ring, but each of these isomerides was obtained synthetically by independent reactions starting with the *cis*- and *trans*-forms of ethyl *cyclo*hexane-1 : 2-diacetate, respectively. These authors also point

out that the *trans*-configuration in these systems is marked by considerable strain. The anhydrides of *cis*- and *trans-cyclo*hexane-1 : 2-dicarboxylic acid (Windaus and Hückel, *Nachr. Ges. Wiss. Gottingen, Math.-physik. Klasse*, 1920, **11**, ii, 181) also may be considered as examples of the type of dicyclic system which is being discussed in this communication. We are engaged in the attempt to resolve the *cis*- and *trans*-modifications of hexahydrocarbazole into their active components.

EXPERIMENTAL.

A mixture of tetrahydrocarbazole (900 g.), alcohol (1800 c.c.), concentrated hydrochloric acid (1800 c.c.), and granulated tin (1800 g.) (compare Borsche, Witte, and Bothe, *loc. cit.*) was heated on the steam-bath for 5 hours, as much alcohol as possible was then distilled off and the residue was poured into beakers and allowed to cool. The product partly solidified to a crystalline mass, which was pulverised, and the whole was then made strongly alkaline by the addition of concentrated aqueous sodium hydroxide. The solid was collected on asbestos, pressed as dry as possible, and then extracted in portions twice with ether. The solid remaining was ground to a paste with more aqueous sodium hydroxide, collected, and again extracted twice with ether. After removal of the ether by distillation, the crude reduction product was crystallised from alcohol and a large quantity of *cis*-hexahydrocarbazole (m. p. 99°) was obtained. By concentrating the mother-liquor three times, further quantities of *cis*-hexahydrocarbazole were obtained. The alcohol was then removed as completely as possible on the steam-bath from the remaining mother-liquor, the residual product dissolved in 60% sulphuric acid, and the solution poured into much water. The small quantity (38 g.) of unchanged tetrahydrocarbazole thus precipitated was removed, and the aqueous solution made alkaline by the addition of concentrated ammonia, which precipitated the crude mixture of the hexahydrocarbazoles as a colourless solid. The product was made into a paste with water, added to an excess of dilute aqueous sodium hydroxide, and shaken with an equal weight (130 g.) of benzoyl chloride. After a few hours, the solid product was collected and crystallised from alcohol; a considerable amount of practically pure 9-benzoyl-*cis*-hexahydrocarbazole then separated. After filtration, the alcoholic mother-liquor was added to an excess of aqueous-alcoholic potassium hydroxide, the mixture boiled under reflux for 3 hours, as much alcohol as possible distilled off, and the residual mixture diluted with water. The sticky product was washed by decantation and crystallised from alcohol; almost pure trans-*hexahydrocarbazole* then separated.

On recrystallisation from alcohol, it was obtained in colourless needles (about 12 g.), m. p. 127° (Found: C, 83·2; H, 8·7; N, 8·1. $C_{12}H_{15}N$ requires C, 83·2; H, 8·7; N, 8·1%). Molecular-weight determinations by Rast's method (*Ber.*, 1922, **55**, 1051) gave for *trans*-hexahydrocarbazole a value of 170 and for the *cis*-form **163**, theory requiring 173. *trans*-Hexahydrocarbazole, like the *cis*-modification, is readily soluble in dilute hydrochloric acid and is reprecipitated on addition of ammonia. Both modifications distilled unchanged: *trans*-, b. p. 286°/769 mm.; *cis*-, b. p. 280°/769 mm.

trans-Hexahydrocarbazole (0·5 g.) and picric acid (0·65 g.) were mixed in hot alcohol; the *picrate* separated, on cooling, in yellow needles, m. p. 179° (Found: N, 13·9. $C_{18}H_{18}O_7N_4$ requires N, 13·9%). The *picrate* of the ordinary *cis*-modification, prepared in the same way, was obtained in yellow needles, m. p. 166° (Found: N, 13·7%).

After *trans*-hexahydrocarbazole had been boiled with an excess of acetic anhydride for an hour, the mixture shaken with much water, and the product crystallised from dilute alcohol, 9-*acetyl*-trans-*hexahydrocarbazole* separated in long, colourless needles, m. p. 113° (Found: N, 6·4. $C_{14}H_{17}ON$ requires N, 6·5%). 9-Acetyl-*cis*-hexahydrocarbazole melts at 98° (Graebe and Adlerskron, *Annalen*, 1880, **202**, 25).

When *trans*-hexahydrocarbazole was made into a paste with water, an excess of dilute aqueous sodium hydroxide added, and the mixture shaken with benzoyl chloride, 9-*benzoyl*-trans-*hexahydrocarbazole* separated; it crystallised from alcohol in colourless needles, m. p. 133° (Found: N, 5·2. $C_{19}H_{19}ON$ requires N, 5·1%). The m. p. of 9-benzoyl-*cis*-hexahydrocarbazole is 106° (Gurney and Plant, this vol., p. 1320).

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CCCLVI.—*The Hydrolysis of Solutions of Sodium Palmitate as measured by Extraction with* p-*Xylene.*

By JAMES WILLIAM MCBAIN and REGINALD BUCKINGHAM.

AFTER long uncertainty and widely conflicting opinions, it is now commonly accepted that the hydrolysis alkalinity of soap solutions is of the order of only $N/1000$ (conductivity: McBain and Taylor, *Z. physikal. Chem.*, 1911, **76**, 179; hydrogen electrode: McBain

and Martin, J., 1914, **105**, 957; catalysis: McBain and Bolam, J., 1918, **113**, 825; Beedle and Bolam, *J. Soc. Chem. Ind.*, 1921, **40**, 27T; ultrafiltration: McBain and Jenkins, J., 1922, **121**, 2325; indicators: McBain and Hay, unpublished). The presence of free fatty acid in all soap solutions is readily demonstrated by shaking them with any suitable solvent such as light petroleum or toluene (Krafft and Stern, *Ber.*, 1894, **27**, 1747, 1755; Krafft and Wiglow, *ibid.*, 1895, **28**, 2566, 2573; Lewkowitsch, *Z. angew. Chem.*, 1907, **20**, 951; Fendler and Kuhn, *ibid.*, 1909, **22**, 107; Holde, *Z. Elektrochem.*, 1910, **16**, 436; S. von Schapringer, Dissert., Karlsruhe, Freiberg, 55—67; Reychler, *Int. Congr. Appl. Chem.*, 1912, **22**, 221), which always extracts fatty acid although the amount is only a small fraction of that which the soap would yield if completely decomposed. As will be seen, such extraction occurs from all soap solutions, whether neutral or containing excess of acid or of alkali. In every case, likewise, the solutions are definitely alkaline even when as much as a complete equivalent of excess of fatty acid has been added to the soap.

Even now, however, the statement is frequently made that soap solutions contain emulsified free fatty acid. This is never true. In spite of the low solubility of the higher fatty acids, there is never enough free fatty acid to saturate the solution, much less to give an excess. If the aqueous layer is saturated with fatty acid, then any non-aqueous layer in equilibrium with it would also be saturated, but in no case has this been observed.

The higher fatty acids must be almost as strong as acetic acid, as is evident from a study of the dissociation constants of the lower acids of the homologous series. The only reason why soap solutions are appreciably hydrolysed is that the free fatty acid formed by hydrolysis is almost wholly removed from solution in the form of acid soap. Such acid soaps form a conspicuous, but often almost unweighable, sediment in dilute soap solutions, and the gross composition of these sediments has often been determined (see McBain and Taylor, *loc. cit.*; Krafft and Stern, *loc. cit.*; McBain, Taylor, and Laing, J., 1922, **121**, 621; McBain and Stewart, this vol., p. 1392), although the elucidation of their exact constitution awaits more rationally planned experiments. There is no similar outlet for the alkali formed by hydrolysis, and it therefore accumulates in the solution. The hydrolysis alkalinity, *i.e.*, the concentration of free hydroxyl ions, is therefore always much greater than the mere trace of free fatty acid present in the solution. Addition of a very small amount of alkali scarcely increases the hydrolysis alkalinity, because it is compensated by removal of acid soap.

It is evident, therefore, that extraction with solvents does not

measure the hydrolysis alkalinity, but that when equilibrium is attained the concentration of the free fatty acid in true solution in the final aqueous layer is indicated. The value of the distribution ratio is such that the concentration of fatty acid in the non-aqueous layer is of the order of 10^6 times greater than that in the aqueous layer. Two kinds of experiments may be carried out, *viz.*, those in which soap solutions are extracted with solvent and therefore changed in composition, and those in which approximately the right amount of fatty acid is previously added to the non-aqueous layer, so that the final equilibrium is determined without appreciable alteration of the aqueous solution. Both methods have here been adopted. When a large excess of fatty acid is added in advance to the non-aqueous layer, it passes into the soap solution, thus again demonstrating the formation of acid soap, since the non-aqueous layer is left unsaturated. It is important that true reversible equilibrium between the two layers was readily obtained in our experiments; the position of equilibrium was obtainable from both sides and did not alter with time at 90°.

Experimental.

All the work was carried out at Bristol University. Mr. H. H. Cole studied toluene, xylene, and deca- and tetra-hydronaphthalene with a view to find a solvent which would fulfil the following conditions: it should be (1) of fairly high boiling point, (2) non-miscible with water, (3) a non-solvent for soap and sodium hydroxide, and (4) only a moderate solvent for fatty acid, which should dissolve as unassociated molecules. He found that the solubility of palmitic acid in twice-distilled *p*-xylene (b. p. 137—138° under 760 mm. pressure) was 33·8 g. in 100 g. of *p*-xylene at 50° and 73·5 g. at 90°, and ebullioscopic measurements showed that the fatty acid was mainly present as simple molecules (Found: *M*, 322, 322, 328, 336. Calc.: 266), but the boiling point constant was found only by calculation. Blank experiments showed that if 9·5 g. of palmitic acid were added to 12 c.c. of xylene, the residue after evaporation showed a loss of only 0·1—0·2 mg. of the acid. Further, xylene was found to dissolve only 0·06% of its weight of sodium palmitate when shaken at 95—97° for 22 hours, thus showing that for the purpose of the present experiments sodium palmitate is insoluble in xylene.

The method here employed is substantially that developed by Miss A. M. King. The greatest practical difficulty is due to the extreme readiness with which these soap solutions become more or less permanently emulsified with the xylene layer, so that separation for analysis becomes impossible. This was finally avoided by carrying out the extraction in horizontal sealed tubes, about

23 cm. long and 1·3 cm. in diameter, tied parallel to the axis of a slowly rotating horizontal stirrer making 20—60 revs. per min. Even under these conditions, if the tubes contained a very large excess of fatty acid or nearly enough salt to salt out the soap, frothing occurred extensively. Between 7000 and 8000 revs. were allowed for attainment of equilibrium, and after 15 minutes' further standing the xylene layer was usually quite clear. Thereupon, the top of the tube was cut off without removal from the thermostat, and as much as possible of the xylene layer was drawn off and weighed; the xylene was then evaporated at 80°, a tube attached to a filter-pump being kept near the surface of the solution in an evaporating dish to renew the air. After 2 hours' drying the residue of fatty acid was weighed.

Two specimens of sodium palmitate, specially made for us by Kahlbaum, were employed. Specimen A contained 4·5% of water and an excess of alkali amounting to 0·0001 equiv. of sodium per equiv. of soap. Specimen B contained 3·47% of water and 0·0008 equiv. excess of sodium. These amounts of alkali and water are allowed for in recording the composition of the solution. All solutions were made with boiled-out conductivity water (1×10^{-6}) in Jena glass flasks. In experiments involving excess of fatty acid or alkali, palmitic acid ("Kahlbaum") or drippings from sodium, free from carbon dioxide, were used, respectively. The salts used were Kahlbaum's "for analysis," dried at 120—130°. Sodium carbonate was heated to bright redness in a platinum crucible for 3 hours. In each case it was found that the salts were insoluble in xylene. All solutions were made up by weight, and concentrations are expressed in weight normality (equivs. per 1000 g. of solvent, water, or xylene). About 7 c.c. of soap solution were used in each experiment. In all cases the temperature was 90° ±0·1°.

Results.

Proof that True Equilibrium is attained.—In order to attach significance to the results, it is necessary to demonstrate that true reversible equilibrium is attained between the two phases. This is conclusively shown by the experiments in Table I, in which identical results were obtained from two series of experiments approaching equilibrium from opposite sides. In the first series, a 0·0774N_w-solution of sodium palmitate was shaken with an approximately equal quantity of pure xylene. In the second series, a 0·0774N_w-solution of sodium hydroxide was shaken with an equivalent quantity of palmitic acid dissolved in xylene. In the first series, after equilibrium had been attained, 17·1% of the total palmitate radical in the system was present in the xylene layer as

palmitic acid. In the second series, 17·3% of the original palmitic acid was finally left in the xylene layer, the remainder having gone into the aqueous layer to react with sodium hydroxide. Thus for the first time it is shown that true equilibrium can be attained in suitably planned experiments on the extraction of soaps.

TABLE I.

Proportion of total palmitate radical extracted when equal weights of 0·0774N_w*-aqueous solution of sodium palmitate and* p*-xylene are brought into equilibrium at* 90°.

Aqueous layer.			Xylene layer.		
N_w-Soap * before.	N_w-NaOH before.	N_w-NaOH † after.	N_w-HP ‡ before.	N_w-HP § after.	% Total HP extracted.
0·0774	0	0·01326	0	0·01262	17·28
0·0774	0	0·01384	0	0·00841	18·01
0·0774	0	0·01257	0	0·01659	16·33
0·0774	0	0·01056	0	0·01397	17·33
0·0774	0	0·01338	0	0·01587	17·43
0·0774	0	0·0100	0	0·01650	16·43
0	0·0774	0·0138	0·0774	0·0138	17·81
0	0·0774	0·0129	0·0774	0·0129	16·69

* Specimen A.

‡ HP = palmitic acid.

† The numbers recorded do not include the hydrolysis alkalinity due to the soap, but only the excess of sodium hydroxide left in the soap solution corresponding with the palmitic acid extracted. The total final alkalinity is not the sum of the original and that shown, because some of the acid extracted comes from acid soap.

§ A saturated solution would be 2·93N_w-palmitic acid.

In order to determine the effects of varying the concentration of soap and the amounts of the aqueous and xylene layers, data are given in Table II for the proportion of the total palmitate radical present in the system which is finally found as palmitic acid in the xylene layer when neutral soap solutions are shaken with xylene.

In all the foregoing experiments the soap solution is robbed of part of its palmitic content by the xylene. Hence the experiments in Table III were carried out by adding excess of palmitic acid to the original xylene, various concentrations being tried until palmitic acid was neither given up to nor extracted from the soap solution. This not only yields the concentration of palmitic acid that is in equilibrium with the unaltered soap solution, but it also affords conclusive proof that true reversible equilibrium was attained in these experiments. The results are plotted in Fig. 1.

Increased experimental difficulties are encountered when the concentration of palmitic acid in xylene exceeds 0·25N_w, *i.e.*, 6% : it was difficult to effect complete evaporation of the xylene if the

TABLE II.

Proportion of total palmitate extracted as palmitic acid when p-*xylene is shaken with aqueous solutions of sodium palmitate at* 90°.

N_w-NaP * before.	Soap soln. (g.).	N_w-NaOH † after.	Xylene (g.).	N_w-HP ‡ in xylene.	% HP extracted.
0·1388	5·2069	0·00684	9·0303	0·01145	4·92
0·1388	6·8610	0·00716	9·0818	0·00915	5·16
0·1388	5·3660	0·00687	7·9261	0·00979	4·94
0·1388	7·4565	0·00793	8·3362	0·00855	5·58
0·1388	6·4728	0·00834	7·7412	0·00857	5·97
0·1118	6·844	0·0109	8·82	0·00821	9·78 §
0·1118	9·396	0·0095	8·82	0·00982	8·50 §
0·1118	7·665	0·0116	8·80	0·00984	10·42 §
0·1096	4·917	0·0144	8·80	0·007877	13·13 §
0·1096	4·501	0·0177	17·60	0·004895	16·15 §
0·1096	4·501	0·0182	17·60	0·004512	16·58 §
0·1096	4·389	0·0177	17·56	0·004295	16·5 §

* Specimen A. † See corresponding footnote in Table I.

‡ A saturated solution would be $2·93N_w$-palmitic acid.

§ Measurements by Miss King, in which the solutions were allowed to stand from 3 to 12 days, thus confirming that time does not appreciably affect the equilibrium at 90°.

TABLE III.

Experiments in which $0·100N_w$-*solutions of sodium palmitate (Specimen B) and water were shaken at* 90° *with xylene to which various amounts of palmitic acid had been added in advance.*

Soap soln. (g.).	Xylene soln. (g.).	HP in xylene. Before, N_w.	HP in xylene. After,* N_w.	Excess in H_2O layer after. NaOH, N_w.	Excess in H_2O layer after. Acid soap, N_w.
5·1691	7·0673	0·1170	0·1217	0·0058	—
4·1934	8·4574	0·1386	0·1385	0·00067	—
6·0092	5·2940	0·1464	0·1452	—	0·0002
4·6990	6·3900	0·1686	0·1655	—	0·0033
6·7521	5·7714	0·1758	0·1704	—	0·0038
5·0572	5·6892	0·1840	0·1790	—	0·0044
5·5903	8·1763	0·1954	0·1909	—	0·0053
5·1498	5·1032	0·2384	0·2310	—	0·0076
4·9988	6·7175	0·9545	0·9371	—	0·0207

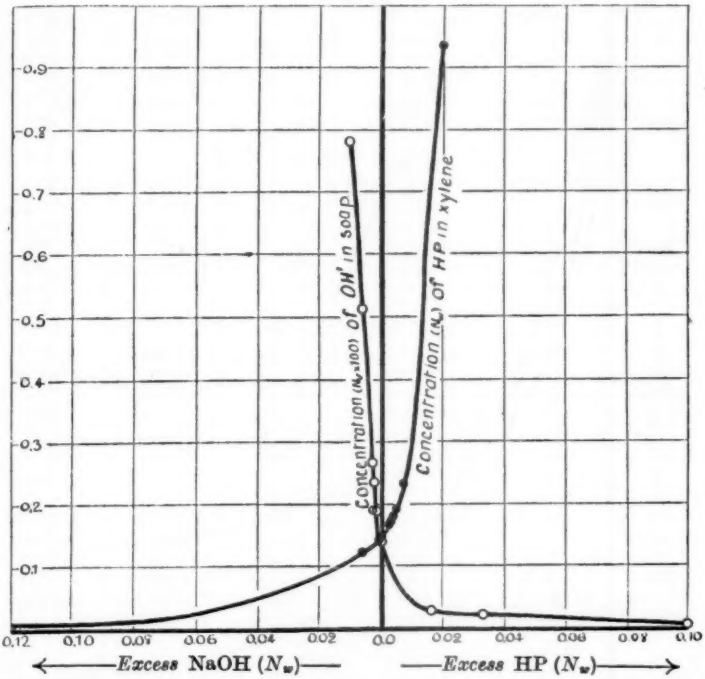
* A saturated solution of palmitic acid would have been $2·93N_w$.

usual amount of solution was used; hence, the solutions were evaporated at 80° under 20 mm. Hg. There is also a strong tendency to emulsification when the xylene contains between 10% and 20% of palmitic acid, but this diminishes again at higher concentrations. The formation of acid soap is indicated by the soap layer becoming absolutely opaque. An experiment with 25% palmitic acid ($0·9545N_w$) is given in Table III and is also included in Fig. 1.

Effect of Electrolytes upon the Extractability.—Table IV and Fig. 2 record experiments in which various pure salts were dissolved in

the $0{\cdot}1N_w$-sodium palmitate solution at 90° before it was shaken with xylene. The salts increased the tendency to frothing, and as the concentration of salt required for salting into two aqueous layers was approached, emulsification became so prominent that the xylene layer finally could not be analysed. The salts made the

FIG. 1.



Hydrolysis equilibria in aqueous sodium palmitate containing excess or deficiency of either sodium hydroxide or palmitic acid. The curve for hydrolysis alkalinity is that obtained by McBain and Martin by the E.M.F. *method. The other curve shows the concentrations of palmitic acid in xylene when the xylene layer is in equilibrium with the soap solution of the final concentration indicated (one experimental point lies off the left of the diagram). Were the palmitate ion constant throughout, the concentrations of hydroxyl ion and of free palmitic acid in the aqueous phase would be inversely proportional to each other.*

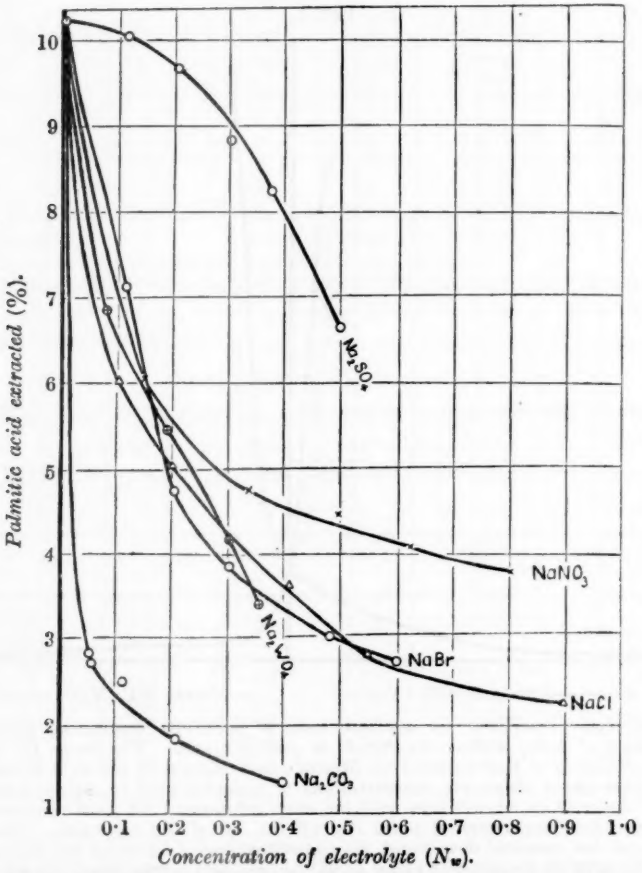
originally clear soap solution cloudy. All the experiments were carried out with Specimen B of sodium palmitate.

Discussion and Interpretation of Results.

The outstanding result of these measurements is that there is scarcely any free fatty acid in a soap solution even when it is appreciably hydrolysed. There is practically quantitative conversion of the fatty acid formed into insoluble acid soap. For

example, a $0{\cdot}1N_w$-solution of exactly neutral sodium palmitate is in equilibrium with the xylene layer containing $0{\cdot}143N_w$-palmitic acid. The saturation concentration or solubility of palmitic acid in xylene is $2{\cdot}93N_w$; hence the xylene layer, and therefore likewise

FIG. 2.



The effect of the addition of salts to aqueous sodium palmitate at 90° upon the amounts of palmitic acid passing into the non-aqueous layer when the soap solution is shaken with an approximately equal volume of p-*xylene.*

the aqueous layer, is not more than 5% saturated with palmitic acid. McBain and Taylor (*loc. cit.*) found the solubility of the undissociated palmitic acid in water at 90° to be $0{\cdot}6 \times 10^{-5}N_w$, and therefore, if the distribution ratio between water and xylene is a constant, the concentration of free palmitic acid in the aqueous layer is only $3 \times 10^{-7}N_w$, whereas the hydroxyl-ion concentration

TABLE IV.

Effect of added salts upon the extractability of $0{\cdot}1N_w$*-sodium palmitate at* 90°.

NaP soln. (g.).	Xylene (g.).	N_w-salt.	N_w-HP in xylene.	% HP extracted.	N_w-NaOH formed.
		Sodium chloride.			
5·3619	5·8108	0	0·00942	10·48	0·0105
5·9920	4·4946	0·1000	0·0112	8·68	0·0086
5·3282	5·0708	0·2000	0·0051	4·96	0·0050
4·7650	6·1778	0·4110	0·0027	3·61	0·0036
4·7140	6·2668	0·5534	0·0020	2·84	0·0028
5·5412	5·1768	0·8970	0·0024	2·30	0·0023
		Sodium bromide.			
5·3619	5·8108	0	0·0094	10·48	0·0105
4·0070	4·8030	0·115	0·0058	7·1	0·0071
6·6604	8·4060	0·204	0·0041	4·4	0·0053
4·5606	6·3834	0·300	0·0034	3·83	0·0048
4·6928	6·1300	0·478	0·0023	3·0	0·0038
4·2768	8·4032	0·600	0·0013	2·67	0·0027
		Sodium sulphate.			
5·3619	5·8108	0·0	0·00942	10·48	0·0105
4·8294	6·3338	0·1145	0·00745	10·05	0·0105
6·3770	5·0828	0·206	0·01204	9·837	0·0098
4·9878	5·4478	0·30	0·00813	8·8	0·00913
5·6500	5·7562	0·376	0·0079	8·34	0·0083
5·7488	6·3568	0·50	0·0058	6·62	0·0066
		Sodium carbonate.			
5·3619	5·8108	0·0	0·00942	10·48	0·0105
6·2130	5·3842	0·100	0·0031	2·8	0·0028
5·8700	6·6298	0·109	0·0023	2·7	0·0027
6·2370	7·4788	0·231	0·0021	2·47	0·00248
5·3062	7·6776	0·417	0·0012	1·80	0·0019
5·4568	7·7641	0·811	0·00086	1·27	0·0012
		Sodium nitrate.			
5·3619	5·8108	0	0·009423	10·48	0·0105
5·5170	5·1642	0·1622	0·0062	5·98	0·0060
5·2456	6·5292	0·337	0·0037	4·70	0·0047
5·5046	6·642	0·475	0·0061	4·4	0·0042
4·606	8·2568	0·634	0·0022	4·0	0·0026
4·8728	6·945	0·809	0·0025	3·72	0·0037
		Sodium tungstate.			
5·3619	5·8108	0	0·00942	10·48	0·0105
5·5227	5·4125	0·1590	0·0067	6·8	0·0068
5·6696	5·2544	0·3828	0·0057	5·4	0·0054
4·2324	5·5602	0·6018	0·0052	4·1	0·0070
5·0958	7·4986	0·7152	0·0022	3·36	0·0034

or hydrolysis alkalinity is $0{\cdot}0013N_w$, as found by several independent methods. Hence, all the palmitic acid representing the difference between these two numbers is removed from solution in the form of acid soap.

It is possible from the data of McBain and Taylor to predict

what concentration of palmitic acid should have been found in $0{\cdot}1N_w$-aqueous sodium palmitate at 90°. Taking the dissociation constant of palmitic acid as 1×10^{-5}, that of water as 33×10^{-14}, the concentration of simple palmitate ion in the solution as $0{\cdot}035N_w$, and the concentration of hydroxyl ion as $0{\cdot}0013N_w$, one can predict the concentration of palmitic acid as $9 \times 10^{-7}N_w$. The $3 \times 10^{-7}N_w$ was estimated above on the assumption that palmitic acid has the same solubility in pure water as it has in $0{\cdot}1N_w$-sodium palmitate saturated with xylene; this is probably not quite correct and may account for the small discrepancy.

The possible influence of salts upon the distribution coefficient, and still more upon the degree of insolubility of acid soap, constitutes the chief uncertainty in interpreting the results in Table IV and Fig. 2. It is clear that the addition of salts to the soap solution diminishes the extractability and probably the hydrolysis, although this should be checked by direct measurement of hydrolysis alkalinity. All these soap solutions were rendered alkaline by the abstraction of palmitic acid, those containing most salt being least affected and yet giving up least palmitic acid. The behaviour of all salts is very similar with the exception of sodium carbonate and sodium sulphate; the difference in the case of the former is clearly due to its alkalinity, but no explanation is forthcoming as to the peculiar shape of the curve for sodium sulphate unless the salt was slightly acid, which was not tested at the time. The effect of the various salts bears no relation to their effect upon salting out of soaps, to the Donnan equilibrium, or to the Hofmeister series, and shows no influence of valency, because all the salts replace each other mol. for mol. with the exception of the carbonate and sulphate. The effect is undoubtedly due to diminution in the concentration of simple palmitate ion (the substance that hydrolyses) and its replacement by colloid. The same explanation would account for the rapid fall in the % hydrolysis with increasing concentration of soap as is illustrated in Table II; 17% of the total palmitate in $0{\cdot}0774N_w$-solution was extracted by an equal amount of xylene, whereas from a solution of twice the concentration only 5% was extracted.

In conclusion, attention may be directed to the series of buffer reactions which occur within a soap solution and render its hydrolysis alkalinity less dependent upon extraneous additions than is usually the case with standard buffers. For example, large change of concentration of the soap, addition of acid or even of a small amount of alkali, and variation of the amount of any non-aqueous solvent with which the solution is shaken all effect only a small change in the concentration of hydroxyl ion. The hydrolysis is chiefly regulated by the insolubility of the acid soap, which is

greatest for the highest fatty acids and distinctly less for unsaturated fatty acids. Further experimental work is now in progress at Stanford University.

Summary.

1. Contrary to the opinions hitherto expressed by most writers, no soap solution contains more than the merest trace of uncombined fatty acid, and even that is completely dissolved, none being in the emulsified or free condition. Thus, in spite of the sparing solubility of the higher fatty acids, soap solutions are unsaturated with respect to them. This is conclusively proved by the fact that any non-aqueous solution brought into equilibrium with an aqueous soap solution is very far from being saturated with fatty acid, even when a large excess of the acid has originally been added to the system.

2. Practically all of the fatty acid corresponding to the hydrolysis alkalinity is locked up in combination as (insoluble) acid soap. Soap solutions are excellent buffers.

3. Electrolytes, even up to high concentrations, diminish the extractability, and probably the hydrolysis, of dissolved soap.

STANFORD UNIVERSITY, CALIFORNIA. [*Received, August 18th,* 1927.]

CCCLVII.—*The Effect of Electrolytes upon the Viscosity of Solutions of Sodium Palmitate.*

By JAMES WILLIAM MCBAIN, HERBERT JAMES WILLAVOYS, and HAROLD HEIGHINGTON.

MANY investigators have studied the viscosity of soap solutions and the effect of electrolytes thereon (Mayer, Schaeffer, and Terroine, *Compt. rend.*, 1908, **146**, 484; Bottazzi and Victoroff, *Atti R. Accad. Lincei*, 1910, (v), **19**, i, 659; Farrow, J., 1912, **101**, 354; Goldschmidt and Weissmann, *Z. Elektrochem.*, 1912, **18**, 380; *Koll. Z.*, 1913, **12**, 18; *Seifensieder Ztg.*, 1913, **40**, 263; Hatschek, *Koll. Z.*, 1913, **12**, 238; *Trans. Faraday Soc.*, 1913, **9**, 80; Kurzmann, *Koll.-Chem. Beih.*, 1914, **5**, 427; Arndt and Schiff, *ibid.*, 1914, **6**, 201; Goldschmidt, *Seifensieder Ztg.*, 1914, **41**, 337; Fischer and Hooker, *Chem. Eng.*, 1919, **27**, 223; Clarke, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **6**, No. 1, 1; King, *J. Soc. Chem. Ind.*, 1922, **41**, 147T; Bircumshaw, J., 1923, **123**, 91; Prasad, *J. Physical Chem.*, 1924, **28**, 636; Freundlich and Schalek, *Z. physikal. Chem.*, 1924, **108**, 153; Freundlich and Kores, *Koll. Z.*, 1925, **36**, 241; Jajnik and Malik, *ibid.*, p. 322; Hahne, *Z. deut. Oel-Fett Ind.*, 1925, **45**,

245, 263, 274, 289, 308), but their work has always been broken off in the region where the viscosity was rising rapidly with increasing concentration of added salt. It remained for Miss A. M. King, in a communication from Bristol University (*J. Soc. Chem. Ind.*, 1922, **41**, 147T), to discover the remarkable fact that further addition of salt produces a sharp maximum of viscosity, which thereafter falls rapidly with still further addition. The last effect continues right up to the limit of possible existence of the soap solution as a single homogeneous phase. The present paper gives further information with regard to this effect (see, *e.g.*, Fig. 1).

Solutions of sodium palmitate at 80° and 90° were chosen for study because of the large amount of other information already available, and also because their properties are independent of time at these high temperatures.

Once again it is shown that, if sufficient care is taken to control the factors involved, even such a property as the viscosity of soap solution is definite and reproducible. For example, we have taken the viscosity of a solution $0{\cdot}5N_w$ with respect to both sodium chloride and sodium palmitate at 81·0° as a point of reference. Miss King published the values for its absolute viscosity in c.g.s. units, $\eta = 10{\cdot}63$ and 10·54; one of us (H. J. W.) obtained 10·07, another (H. H.) 10·06, and Mr. H. Horwood 10·39, all with different specimens of pure sodium palmitate. In other series of experiments, the viscosity of the original soap solution was first taken, then successive amounts of pure electrolyte were added, thus giving a range of viscosity readings up to the limit of existence of isotropic soap solutions. Thereupon, the final solution was diluted with successive portions of the original soap solution, retracing the curve, and yielding confirmatory values.

For details of the experimental method reference may be made to the communication cited. A Wenner stop-watch reading to 0·01 sec. was employed. Temperatures were read on standardised thermometers. The steel balls required were heated before being dropped through the tube in order to avoid solidification of the soap solution on them. All concentrations are expressed in weight normalities (N_w), *i.e.*, g.-mols. per 1000 g. of water.

The results were calculated according to the formula $\eta = K(s - D)T$, where K is the tube constant $\eta_1/(s - \sigma)T_1$, η is the viscosity of the soap solution in c.g.s. units, D its density, s the density of the steel ball, T and T_1 are the times of fall in soap solution and castor oil respectively, η_1 is the viscosity of castor oil = 16·46 c.g.s. units at 14·1°, and σ the density of castor oil = 0·963. The value of K depends upon the dimensions of the tubes and balls, and the values used are given in Table I.

TABLE I.

Calibration of the falling balls and tubes with castor oil (Kahlbaum).

Observer.	Temp.	Diam. of steel balls.	Density of balls.	T_1 (secs.).	Tube constant, K.
Horwood	14·1°	0·316 cm.	7·595	6·0	0·4136
,, ...	14·1	1/8 in.	7·720	6·2	0·3928
Heighington	14·1	1/8 in.	7·697	6·2	0·3943
Willavoys	15·7	0·163 cm.	7·554	29·32	0·0731

The results for 0·75, 1·0, and 1·5N_w-solutions of sodium palmitate with added sodium chloride are in Table II. The 1·5N_w-solutions are so viscous that for determining the density a specially wide pipette was employed, closed at the bottom with a flattened glass rod held in place by rubber tubing, and continued at the top with a small tube also held in place by rubber tubing so that when temperature equilibrium was attained this could be slipped off, leaving the pyknometer exactly filled with soap solution. Thereupon the tube was cooled and the contents were solidified for weighing.

Results for approximately 1·5N_w-sodium palmitate with added sodium carbonate or acetate at 81° are given in Table III.

Discussion.

The experimental results for added sodium chloride at 81° are shown in Fig. 1 and those for the acetate and carbonate in Fig. 2. The outstanding effect is that the addition of medium concentration of electrolyte enormously increases the viscosity of soap solution. Without salt, the viscosity is only a few centipoises, and it is increased 600—700-fold at the maxima by the addition of the salt. It may be recalled that with many soaps at lower temperatures the soap solutions in these intermediate concentrations of salt actually set to a jelly, but the effect there also passes through a maximum, and further addition of salt reliquefies the jelly.

The most striking feature of the curves is the existence of these sharp maxima at which the effect of salts is reversed, the viscosity with further increase of salt falling off as rapidly as it had risen. For example, in the curve for carbonate (Fig. 2) the highest viscosity measured was 102 poises, which fell on further addition of carbonate to 6 poises. With the most concentrated soap and sodium chloride, the fall is from 55 to 3 poises. The limited extent of the fall is, however, shown by the fact that when the soap solution contains all the salt that can be added without the formation of several layers, the viscosity is still 20—50 times higher than that of the original soap without salt.

Table II.

Viscosity and density of solutions of sodium palmitate containing various weight normalities of added sodium chloride at about 81·0°.

Observer.	Temp.	NaCl (N_w).	T (secs.).	Density (g./c.c.).	η.
		0·75N_w-Sodium palmitate.			
Horwood	81°	0·729	2·5	0·992	6·82
,, ...	,,	0·600	5·3	0·991	14·48
,, ...	,,	0·748	2·4	0·991	6·34
H. H.	,,	0·201	0·9	0·977	2·38
,, ...	,,	0·400	7·6	0·9850	20·11
,, ...	,,	0·500	6·99	0·9877	18·49
,, ...	,,	0·300	3·39	0·9823	8·96
,, ...	,,	0·600	5·2	0·9900	13·75
,, ...	,,	0·450	8·718	0·9864	23·07
H. J. W.	,,	0·440	57·74	0·981	27·74 *
,, ...	90	0·880	1·79	0·9872	0·73 †
		1·0N_w-Sodium palmitate.			
H. H.	81·00	0·880	0·98	1·00000	2·59
,, ...	81·26	0·6797	3·06	0·99805	8·08
,, ...	81·7	0·5771	5·42	0·99570	14·4
,, ...	81·63	0·46945	7·3	0·98805	19·3
,, ...	81·64	0·50000	7·24	0·98980	19·1
,, ...	81·65	0·37220	9·95	0·98645	26·3
,, ...	81·68	0·26205	11·23	0·98310	29·7
,, ...	81·76	0·14445	4·17	0·97910	11·0
,, ...	81·7	0·29000	10·47	0·98310	27·7
,, ...	81·7	0·25000	7·7	0·97530	20·4
,, ...	81·7	0·32000	11·1	0·98470	29·4
H. J. W.	80·96	0·3000	68·76	0·9826	33·0
,, ...	90·05	0·3000			10·2
H. H.	81·92	0·1445	4·76	0·9791	12·3
		1·50N_w-Sodium palmitate.‡			
H. J. W.	80·97	0·100	88·21	0·9740	39·54
,, ...	80·95	0·7500	11·60	1·005	5·55
,, ...	80·99	0·8700	6·45	1·016	3·08
,, ...	81·01	0·7120	12·45	1·001	5·96
,, ...	81·00	0·5658	26·06	0·9965	12·48
,, ...	90·06	0·4395	17·16	(0·9851)	8·24
,, ...	81·01	0·4395	41·53	0·9851	19·94
,, ...	81·03	0·3015	71·03	0·9614	34·23
,, ...	90·05	0·2660	29·75	0·9614	14·33
,, ...	81·00	0·2660	75·78	0·9458	36·59
,, ...	81·00	0·2431	85·38	0·9806	41·02
,, ...	80·99	0·2032	102·77	0·9651	49·49 §
,, ...	81·01	0·1845	105·27	0·9642	50·71 §
,, ...	81·00	0·1459	109·43	0·9692	52·65 §
,, ...	80·98	0·1049	83·48	0·9800	40·12
,, ...	80·94	0·08076	67·77	0·9740	32·59
,, ...	80·98	0·06503	83·32	0·9700	40·09
,, ...	81·02	0·04287	83·58	0·9600	40·28

* High value owing to slight fall in temperature.

† At 90°, hence about 2·2 at 81°.

‡ 1·5N_w-Sodium palmitate does not exist as a single homogeneous solution at 81°, but falls in the heterogeneous region—middle soap + isotropic solution (see McBain and Langdon, J., 1925, **127**, 863).

§ Small crystals developed (acid sodium palmitate).

TABLE III.

Viscosity and density of solutions of sodium palmitate containing various weight normalities of added salts at about 81°.*

Temp.	Added salt (N_w).	T (secs.).	Density (g./c.c.).	η.
	1·491N_w-Sodium palmitate with addition of sodium carbonate.			
81·05°	0·1876	213·3	(1·000)	102·2
81·09	0·4764	108·0	1·016	51·50
80·99	1·2736	26·8	(1·000)	12·84
80·99	1·6228	12·54	(1·000)	6·01
	0·1000	Heterogeneous—two layers.		
	1·47N_w-Sodium palmitate with addition of sodium acetate.			
81·01	0·09786	90·82	0·9712	43·69
81·02	0·1490	118·85	0·9815	57·12
81·02	0·2081	128·97	0·9825	61·95
81·01	0·2759	67·23	0·9842	32·28
81·00	0·3958	27·50	0·9851	13·20
	0·5837	Heterogeneous system—nigre and lye.		

* Experiments by H. J. W.

The higher the concentration of soap, the less salt is required to produce the maximum viscosity, as the following tabulation shows :

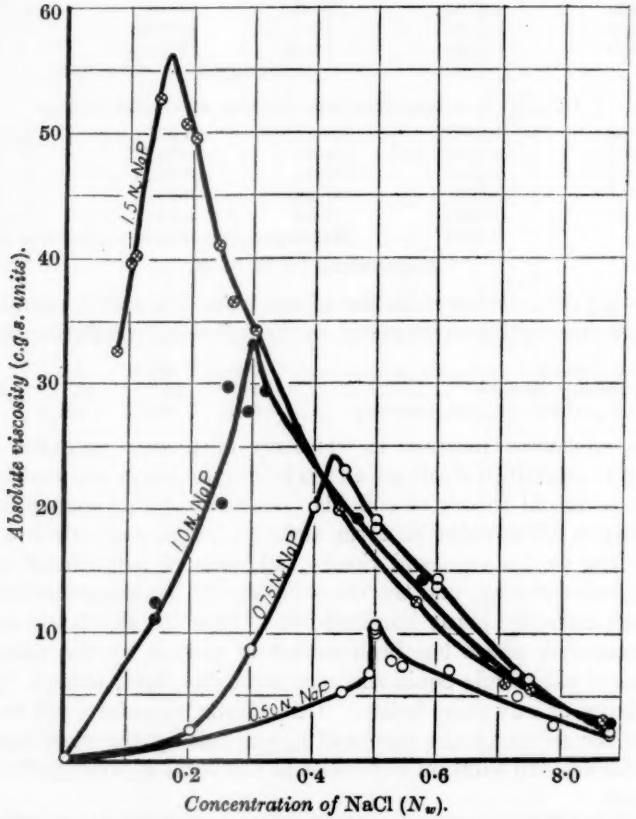
Conc. of soap (N_w)	0·5	0·75	1·0	1·5
Max. viscosity (poises)	10	24	33	56
Conc. (N_w) of salt at max. viscosity	0·50	0·43	0·30	0·16

The enormous increase in viscosity of a soap solution when moderate quantities of salt are added to it again shows the inadequacy of the emulsoid theory of colloids. In these strong soap solutions the soap is all in colloidal form already, before any salt is added. According to the emulsoid theory, addition of salt should shrink the globules of soap, and the viscosity should be diminished instead of being increased many hundred-fold. That the salt is less soluble in a soap-rich phase has been definitely proved by the numerous studies of phase-rule equilibria now available, and, indeed, by the experience of any soap boiler. This affords, therefore, yet another reason for replacing the emulsoid hypothesis by the view that the colloidal soap in solution is present in the form of solid particles or micelles.

Superficially, the curves look like any of Loeb's for the Donnan equilibrium. However, they differ in two respects. In the first place, Loeb's experiments never involved more than a five-fold increase in viscosity, whereas these involve increases of a higher order of magnitude. In the second place, Loeb's maxima arose from the fact that he was adding an acid or an alkali to an amphoteric colloid and producing colloidal electrolyte with high conductivity, osmotic activity, etc., whereas here, salts are being added and should have a uniformly depressing action on the viscosity, as was indeed observed by Loeb for salts when added to the systems he studied.

The problem then is to explain why fully formed colloid may have its viscosity increased many hundred-fold through the addition of salt. The only possible explanation seems to be the general hypothesis advanced by one of us (McBain, *J. Physical Chem.*, 1926, **30**, 239), that the viscosity of a reversible colloid, such as nitro-

FIG. 1.



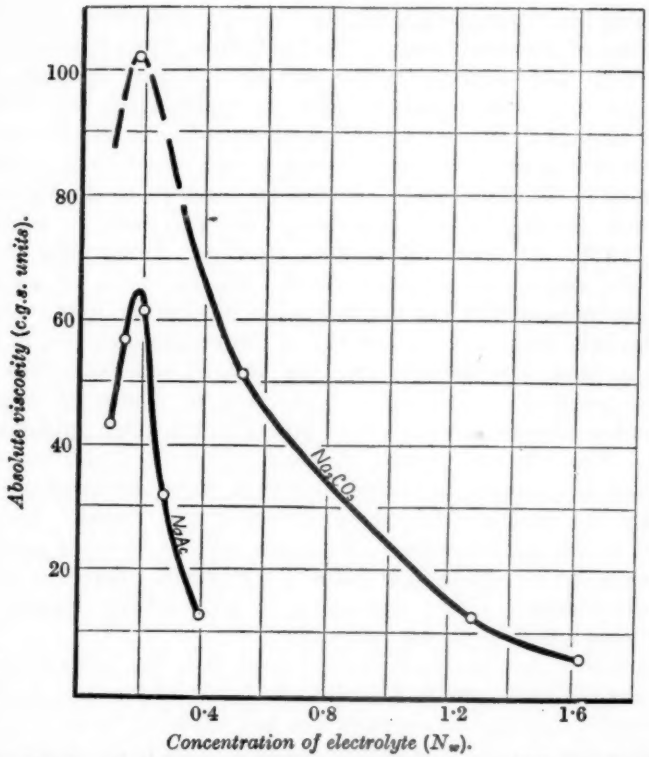
The viscosity of solutions of sodium palmitate at 81° *as affected by addition of sodium chloride up to the maximum amount which can be added without salting out the solution into two layers.*

cotton, soap, rubber, or protein, is not to be accounted for by the individual particles (micelles) either through their number or individual bulk, but that it is due to their loose aggregation into structures which effectively enmesh large tracts of the solvent or solution.

Hatschek (*J. Physical Chem.*, 1927, **31**, 353) has recently published a communication which is ostensibly an attack upon McBain's

general hypothesis of aggregation, but which is really an adoption and endorsement of one particular form of the general hypothesis, being a modification of that of Loeb. In general, there is a great variety of possible forms of aggregation. For example, if all the particles were to be joined end to end to form innumerable filaments, the medium in which they lay could be so effectively enmeshed as to

FIG. 2.



The viscosity of solutions of $1{\cdot}5N_w$*-sodium palmitate at* 81° *over the whole range of existence of isotropic solution in the presence of sodium acetate and sodium carbonate, respectively.*

have the properties of a jelly. Another form of loose ramifying aggregation is that of a pile of brushwood, or again seaweed in a rock pool. Hatschek would prefer to specify only one kind of ramifying aggregate like a lot of separate bushes not entangled but separate from each other, so that each aggregate could be treated approximately as a polyhedron, or even as a sphere. To call this loose ramifying aggregate the micelle is to introduce fresh confusion into the subject. We should prefer to retain the general hypothesis,

which includes Hatschek's as one possibility. We use the term micelle to indicate each of the single ultimate particles of colloid.

Attention may be directed to another influence which greatly enhances the effect of the presence of either particles or ramifying aggregates in their influence upon the apparent viscosity of the system. Hatschek has demonstrated that even in a suspension in which aggregation does not occur and in which hydration in the chemical sense is absent, the system does not show a true viscosity coefficient like a pure liquid, but the viscosity coefficient obtained is a function of the rate of shear. He has been at a loss to account for this effect, and similarly Porter and Rao (*Trans. Faraday Soc.*, 1927, **23**, 311) were unable to offer an explanation, but made a purely empirical attempt to obtain an equation to fit the results. As part of a general theorem relating to the structure of surfaces, one of us (J. W. McB.) and G. P. Davies (Address to the Mid-West Regional Meeting of the American Chemical Society, Madison, June, 1926; *J. Amer. Chem. Soc.*, 1927, **49**, 2230) have shown that this effect is a necessary result. On the basis of accurate absolute measurements on the amount of adsorption, now available for the first time, and of a survey of the results obtained in such fields as that of adhesives, etc., the authors concluded that any surface possesses considerable depth due to chains of oriented molecules extending inwards from points on the outer unimolecular layer. The effective length of these chains is conditioned by thermo-vibration and, of course, by rate of shear, the latter accounting for the results obtained by Hatschek and Porter. Hence a liquid in the neighbourhood of surfaces such as those of particles, filaments, or ramifying aggregates is semi-rigid, enhancing greatly the effectiveness of the aggregates in immobilising liquids, and producing a high apparent viscosity.

According to previous studies of soap, it is the neutral micelle, and not the ionic micelle, that has the power of forming ramifying aggregates. Salt does promote the formation of neutral micelles at the expense of ionic micelles, but this effect is too unimportant for our present purpose. We should ascribe the aggregation of the neutral micelles to partial dehydration on the addition of salt owing to the lowering of the vapour pressure of the solution. This is the first main factor involved in the action of salts upon soap solutions.

The maximum and the subsequent lowering of viscosity have still to be explained, and any explanation has to be sufficiently general to account for the salting out and phase-rule equilibria of soap, together with the formation of liquid crystals. We would seek this in a combination of the principles of dehydration through lowering

of vapour pressure (as above), of orientation of like molecules when held sufficiently close together, and of the principle underlying the Donnan equilibrium. The dehydration facilitates aggregation by exposing unsaturated valence bonds (compare McBain, *J. Physical Chem.*, *loc. cit.*), thus tending to make the aggregates denser and less voluminous. The principle of constancy of ionic product, as exemplified by solubility of precipitates, utilised by Donnan and generalised by Wilson, must now be made use of to explain further the effect of salts upon the charges and the volumes within the colloidal aggregates.

Almost all surfaces, even those of the neutral micelles, show slight electrical charges (see Laing, *J. Physical Chem.*, 1924, **28**, 673). Particles of like charge tend to repel each other, probably not merely through direct electrostatic repulsion (the usual belief), but also through the excess osmotic pressure set up in the neighbourhood of all charges through the Donnan equilibrium. The effect of large excess of salt is two-fold : first, to reduce these charges, and, secondly, to minimise their effect upon the Donnan osmotic pressure in their neighbourhood. These two influences contribute to the collapse, or rather the closer packing, of the structures built up from the micelles, thus reinforcing the effect of increased intensity of aggregation. This releases a part of the liquid, or better, less of it is immobilised, and hence the apparent viscosity falls. This would appear to explain the decline in viscosity that occurs in more concentrated solutions of salts, whilst still leaving the viscosity higher than that of the original soap solution. This explanation embraces that given by Laing and McBain (J., 1920, **117**, 1507) for the formation of true soap jellies which occur in the middle of the isotropic region and are liquefied by excess of added salt. It should be noted that the curves in Fig. 1 cover practically the whole field of the possible existence of isotropic solutions of sodium palmitate (compare McBain and Langdon, *loc. cit.*). Throughout, the chief factor involved in apparent viscosity of colloids is the extent to which the solution or solvent is immobilised through entanglement in colloidal structures.

When aggregation, brought about through dehydration and segregation as detailed above, becomes extreme, and the micelles are therefore more tightly packed in clumps, the tendency towards orientation must strongly assert itself (orientation of molecules accounts for the existence of micelles in the first place). Excess of salt always produces neat soap and lye, the latter being an ordinary salt solution containing most of the salt and scarcely any soap; the neat soap is liquid crystal. The common feature of all present hypotheses regarding the structure of liquid crystals is that they are

full of tracts in which molecules or micelles are in an approximately parallel arrangement.

Whilst the above description appears to afford a reasonable explanation of the phenomena here discussed, searching tests are required to afford independent proof of the truth of each of the mechanisms involved. Again, far too little is known with regard to the structure of liquid crystals. Indeed, soap solutions afford the only examples of liquid crystals readily accessible for experimental study. The position of middle soap has still to receive adequate explanation. If a soap solution containing no added salt is sufficiently concentrated, middle soap separates as a new phase, and, within a certain range of concentration, soap solutions consist only of this form. Middle soap is a colloidal electrolyte, just like the isotropic solutions it has replaced. A small amount of salt may be added to middle soap, but it is destroyed by further salt, being replaced by isotropic soap solution. This is the significance of the curves for $1{\cdot}5N_w$-sodium palmitate in Figs. 1 and 2, which necessarily have their beginning as shown in the diagrams in the presence of the necessary minimum of salt. The pure $1{\cdot}5N_w$-sodium palmitate is middle soap; it turns into isotropic soap solution upon the addition of the requisite amount of salt, and the viscosity shortly thereafter passes through a maximum as shown in the diagrams. It throws a severe strain upon our explanation (detailed above) to account for these phenomena, because they ended in the production of liquid crystal through excess of salt, with the elimination as a separate phase of most of the water and salt, whereas here the $1{\cdot}5N_w$-sodium palmitate begins as liquid crystal, although retaining all the water with it in one homogeneous phase.

The existence of middle soap as liquid crystal is quite evidently due to mere contiguity of the particles on account of the very high concentration of soap. We have to suppose that this orientation is almost tantamount to coalescence, because no negative ions, other than a trace of hydroxyl ion (and of course the ionic micelles), are present to keep the particles apart. Addition of a small amount of salt supplies this defect, and the tracts of parallel orientation are disbanded with the formation of isotropic solution, although the apparent viscosity is already extremely high and aggregation or linkage is already at an advanced stage. Thereafter, but little salt is required to produce the maximum and the other specified effects.

Comparison of the effects due to the three salts is interesting, but in view of the explanations above it cannot be expected to be of direct significance. The two univalent salts, chloride and acetate, are fairly similar in the position and value of the maximum viscosity,

that for sodium acetate being slightly higher and requiring rather more acetate, sodium acetate being a weaker electrolyte than sodium chloride. The bivalent sodium carbonate gives twice as high a maximum viscosity as the chloride and twice as much of it is required for salting out the palmitate into two layers. However, the acetate is exceptionally effective in salting out, $0{\cdot}57N_w$ being sufficient as compared with $0{\cdot}88N_w$ for the chloride and $1{\cdot}7N_w$ for the carbonate. McBain and Pitter (J., 1926, 893), in comparing a large number of salts, pointed out that apparently the single factor most effective in salting out is the concentration of the sodium ion. We suspect that the high viscosity in the presence of the carbonate may be due to its alkalinity, because we have found with various other samples of sodium palmitate that a slight excess of alkalinity very greatly increases the viscosity. Thus, if the sodium palmitate contains about one equiv. per cent. excess of sodium hydroxide, all the maxima of viscosity are roughly 1·7 times greater.

The futility of attempting to apply any of the usual empirical formulæ to our results is evident from the shape of the curves and also from the fact that the right-hand descending portions of the viscosity curves approximately coincide, *i.e.*, the viscosities are there nearly independent of the amount of soap present.

All the work here described was carried out at the University of Bristol.

Summary.

1. The viscosity of solutions of sodium palmitate has been studied over most of the range of existence of isotropic soap solutions in the presence of sodium chloride, acetate, and carbonate.

2. Addition of electrolytes increases the viscosity to a maximum value many hundred times greater than that of the original soap solution. Further salt decreases the viscosity almost equally rapidly until the salting out concentration is reached.

3. The results are discussed on the basis of the general explanation put forward by McBain for the high apparent viscosity of reversible sols and jellies. The rise in viscosity is in the opposite direction to that predicted by the Donnan equilibrium, and exceeds by a hundredfold the viscosity effects observed by Loeb, although the Donnan equilibrium may well be one of the factors involved.

STANFORD UNIVERSITY, CALIFORNIA. [*Received, August 18th,* 1927.]

CCCLVIII.—*The Composition of Bleaching Powder. Part I.*

By EDMUND ARTHUR O'CONNOR.

THE exact composition of the substances contained in bleaching powder has long been a subject for discussion (see Lunge, "Sulphuric Acid and Alkali," 3rd edn., III, pp. 577—587; Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," II, pp. 262—265), which has centred chiefly around the question of the existence of a definite compound of calcium hypochlorite and calcium chloride in equimolecular proportion, to which was usually assigned the constitution $CaCl{\cdot}OCl$. Basic compounds containing hypochlorite and chloride have also been postulated by several authors. Lunge (*op. cit.*, p. 585) expressed the following opinion: "It is certain that no calcium chloride is present as such in ordinary bleaching powder." Similar views were held by O'Shea (J., 1883, **43**, 410) and by Orton and Jones (J., 1909, **95**, 751).

A study of the literature led to the conclusion that there is no positive evidence for the existence of a compound of calcium hypochlorite and chloride. Such a compound has never been isolated, and the evaporation at low temperature of solutions obtained by extraction of bleaching powder with water led to a separation of crystals of hydrated calcium hypochlorite, reported as $Ca(ClO)_2,4H_2O$ (Kingzett, J., 1875, **28**, 404; Orton and Jones, *loc. cit.*). At the same time, Orton and Jones obtained three crystalline preparations, containing calcium hypochlorite and chloride together with calcium oxide and water, which on analysis yielded a molecular ratio of hypochlorite to chloride of 1 : 1. These substances, which could not be recrystallised from water, were only approximately analysed, owing to the small quantities available and to the difficulty of complete separation from mother-liquor. There is, therefore, no certainty that any of them was a single definite compound, although it appears likely that one or more basic double salts may exist.

The preparation of calcium hypochlorite comparatively free from calcium chloride, and in some cases free from calcium oxide, has been exploited in recent years by the Chemische Fabrik Griesheim-Elektron (B.PP. 17859, 182927, 188662; D.R.-PP. 188524, 195896, 282746). Calcium hypochlorite, prepared by chlorinating a paste of calcium hydroxide and water and removing as much as possible of the mother-liquor, is stated to be a very stable compound when thoroughly dry, and superior in this respect, as well as in available chlorine, to the best ordinary bleaching powder. Basic compounds

containing 1—4 mols. of calcium hydroxide to one of hypochlorite, prepared by a similar process, are claimed to have the same advantages. Two of these compounds, $Ca(ClO)_2,2CaO,2H_2O$ and $Ca(ClO)_2,4CaO,4H_2O$, were isolated, but not in crystalline condition.

The problem of the exact nature and proportions of the substances composing any particular sample of bleaching powder cannot be expected to be capable of solution, for there is no certainty that equilibrium has been established. The equilibrium composition of a bleaching powder giving any particular ultimate analysis (neglecting formation of chlorate) could be determined if data for equilibria in the quaternary system $Ca(ClO)_2$–$CaCl_2$–CaO–H_2O at the same temperature were available. Consequently, it was decided to attempt at a suitable temperature a preliminary investigation of the three ternary systems in which water is a component.

Solutions of hypochlorites decompose rapidly at the ordinary temperature only in the presence of hypochlorous acid, and if this be removed by addition of a slight excess of alkali, the solutions are comparatively stable, forming chloride and chlorate and evolving oxygen very slowly (Foerster and Jorre, *J. pr. Chem.*, 1899, **59**, 53; Foerster, *ibid.*, 1901, **63**, 141). Solutions of calcium hypochlorite which can contain only small concentrations of free hydroxide rapidly increase in stability as the temperature falls, partly because of the usual diminution of reaction rate and partly because less hypochlorous acid is formed by hydrolysis. The whole of the experimental work was therefore carried out at 0°, and in the system $Ca(ClO)_2$–$CaCl_2$–H_2O a minute amount of calcium hydroxide was allowed to be present in the solutions.

Experimental.

A. *Analytical Methods.*—Hypochlorite was estimated by the usual iodometric method, and chloride by the Volhard process if hypochlorite was absent. In the presence of hypochlorite, chloride was estimated by first determining the former, and then finding the total chloride present after the hypochlorite had been reduced by neutral hydrogen peroxide. The same method of reduction was employed when it was necessary to estimate hydroxide in the presence of hypochlorite. The accuracy of these methods was checked by a determination of total calcium by the oxalate–permanganate process in a few control experiments.

B. *The Preparation and Properties of Calcium Hypochlorite.*—The following procedure, based upon the process of the Chemische Fabrik Griesheim-Elektron (*loc. cit.*), was adopted. About 224 g. (4 g.-mols.) of calcium oxide, prepared by ignition of the pure

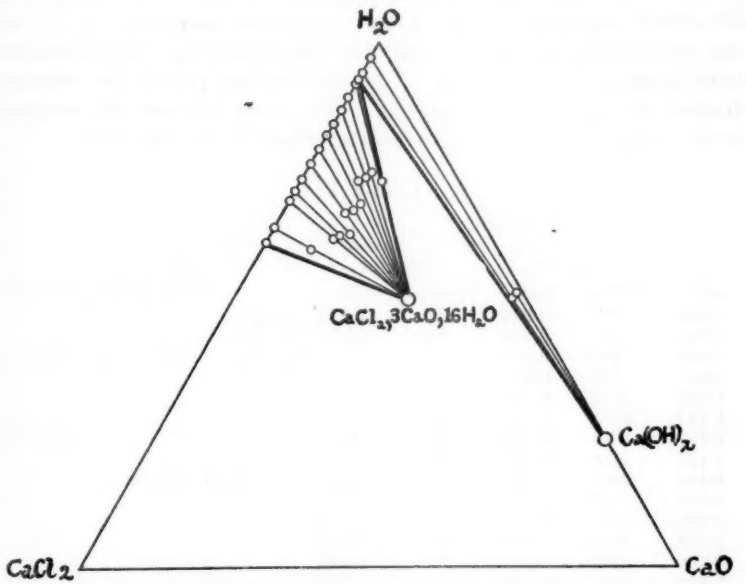
precipitated carbonate, were treated with 650 c.c. of water, whereby a thin paste resulted, quite free from lumps. The cooled paste was introduced into a cylindrical gas-jar provided with a rubber stopper with holes for an inlet tube and a stirrer. The inlet tube reached well down into the jar, and the stirrer, which was of anchor-shape, was made long and wide enough to agitate the whole contents of the cylinder when rotated rapidly by a motor. Chlorine, washed with water, was supplied from a small battery of diaphragm cells, with hydrochloric acid as electrolyte, at an initial rate of about 105 g. per hour. The temperature was allowed to rise to about 40°, external cooling being used when necessary. Under these conditions, there was no visible indication of basic salts, the calcium hydroxide progressively disappearing. After about 70% of the theoretical quantity of chlorine had been admitted, a sudden separation of calcium hypochlorite occurred, and the contents of the flask became pasty once more. The temperature was then reduced to about 25°, and more chlorine was passed in at one-third of the above rate, until from 90% to 95% of the theoretical quantity had been supplied. (After the separation of calcium hypochlorite, chlorine is not absorbed so readily, and a more rapid stream of the gas is partly wasted.) It was not found practicable to chlorinate beyond the limit given, as any further quantity of chlorine caused the complete loss of the preparation by production of free hypochlorous acid.

The paste containing calcium hypochlorite was collected in a Buchner funnel on asbestos-paper, since ordinary filter-paper was rapidly destroyed. The filtration was somewhat slow, but when the characteristically soft mass was covered with asbestos-paper and well pressed, a fair separation from mother-liquor was effected. Comparatively little hypochlorite remained in solution. Further separation of mother-liquor was brought about by pressing the cake of hypochlorite between very thick plates of porous earthenware, specially made for the purpose. After a few hours, the apparently dry substance was desiccated in a vacuum over caustic soda. It formed pale greenish-yellow, almost odourless, apparently non-crystalline lumps, which developed a strong smell of hypochlorous acid on exposure to air.

Pure calcium hypochlorite was prepared by making a saturated solution of the crude product in water and filtering off the insoluble residue of calcium hydroxide or basic salt. The solution was evaporated under the diminished pressure afforded by a water-pump. Concentration progressed until the liquid was considerably supersaturated, and short, needle-shaped crystals finally appeared, at first slowly, then more rapidly. At this stage it was found best

to stop the evaporation, and allow the crystals to be produced without agitation. A more granular product, easily filtered and dried as described above, then resulted. A repetition of the process yielded calcium hypochlorite free from chloride, and therefore free from chlorate. About $\frac{1}{2}$% of calcium hydroxide (or an equivalent quantity of basic salt) was present, rendering unfiltered solutions slightly turbid. Analysis of the final product gave results for hypochlorite and total chlorine which agreed with one another within the limits of experimental error. When thoroughly desiccated, calcium hypochlorite shows no appreciable decomposition

FIG. 1.



after several days, if kept out of contact with air. Concentrated aqueous solutions are greenish-yellow, and decompose at 25—35° at the rate of about 1% per day, evolving a very slow stream of oxygen in minute bubbles. At 0°, there is no decomposition or evolution of oxygen during the period of the experiments.

C. *The System* $CaCl_2$–CaO–H_2O.—This system has already been examined at 10°, 25°, 40°, 48°, and 50° (Milikan, *Z. physikal. Chem.*, 1917, **92**, 59), basic compounds $CaCl_2,3CaO,16H_2O$; $CaCl_2,CaO,2H_2O$; and $CaCl_2.CaO.5(?4)H_2O$ being reported. The third was obtained only at 48° and 50°, whilst the range of existence of the first increases and that of the second diminishes as the temperature falls. The results (Table I and Fig. 1) obtained at 0° show that $CaCl_2,3CaO,16H_2O$

is the only basic salt obtainable at that temperature It forms well-defined, transparent, needle-shaped crystals, which may attain a length of several mm. if the mother-liquor does not contain too much calcium chloride.

Suitable complexes were rotated in a thermostat for about 24 hours, which was found to be a sufficient time for establishment of equilibrium, and the composition of the solid phases was deduced by the residue method. The separation of residues from solutions was achieved in the following manner. The disc of a Gooch crucible was placed in the bottom of a small cylindrical funnel and covered with a pad of asbestos well pressed down, which was then thoroughly dried. The funnel was stoppered loosely, fitted to the neck of a filter-flask connected to the water pump, and immersed in the ice and water of the thermostat, only the top projecting. The filtration could then be carried out at 0°, no matter how slowly the solution drained through the asbestos pad. The same process was adopted in the examination of the two systems about to be described.

TABLE I.

	Composition, %.				
	Solution.		Residue.		
$d_4^{0°}$.	$CaCl_2$.	CaO.	$CaCl_2$.	CaO.	Solid phase.
1·025	2·7	0·214	1·0	46·5	$Ca(OH)_2$.
1·048	5·5	0·226	2·0	46·8	
1·056	6·8	0·216	—	—	$Ca(OH)_2 + CaCl_2,3CaO,16H_2O$.
1·067	7·6	0·212	12·7	13·7	$CaCl_2,3CaO,16H_2O$.
1·089	10·2	0·186	13·5	11·2	
1·111	12·5	0·172	15·0	10·7	
1·133	15·2	0·164	16·6	9·8	
1·155	17·4	0·152	18·4	12·4	
1·186	20·0	0·148	20·2	11·8	
1·213	22·8	0·145	21·8	10·7	
1·240	25·6	0·142	23·0	13·4	
1·265	28·0	0·138	24·9	11·9	
1·280	29·7	0·152	26·1	11·1	
1·338	34·9	0·190	31·0	8·3	
1·370	37·6	—	—	—	$CaCl_2,6H_2O$.

D. *The System* $Ca(ClO)_2$–$CaCl_2$–H_2O.—The investigation of this system presented no special difficulty. When calcium hypochlorite was intended to be present as solid phase, it was added in excess to suitable solutions of calcium chloride. It was necessary to have these solutions, particularly when concentrated, free from calcium hydroxide, otherwise the hydroxide, always present in small amount in solid calcium hypochlorite, was converted into basic chloride, and did not pass entirely into solution. A corresponding error in the composition of the residues, which became slightly too rich in calcium chloride, was then produced.

The experimental figures, reproduced in Table II and Fig. 2,

show definitely that no compound of calcium hypochlorite and calcium chloride can be formed in aqueous solution at 0°, and that the composition of the hydrate of the former salt is $Ca(ClO)_2,3H_2O$, and not $Ca(ClO)_2,4H_2O$ as reported by Kingzett and by Orton and Jones (*loc. cit.*). The solubility of this hydrate in water at 0° is 21·8%.

FIG. 2.

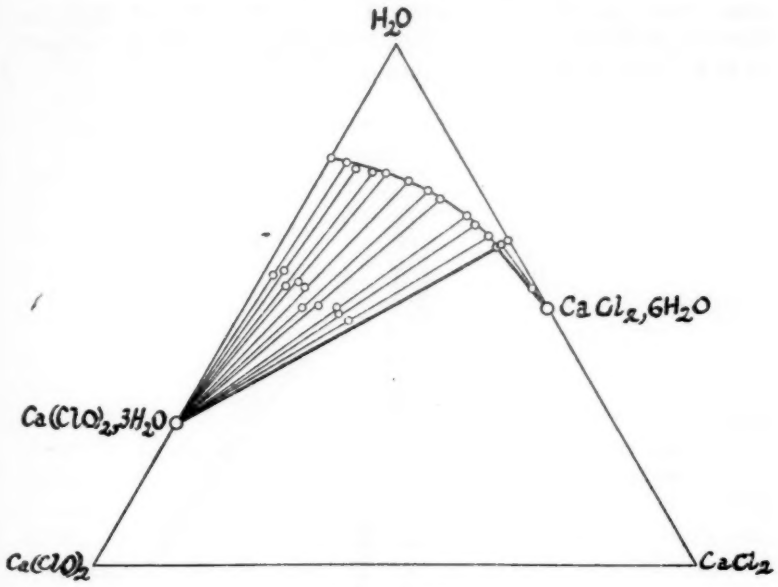


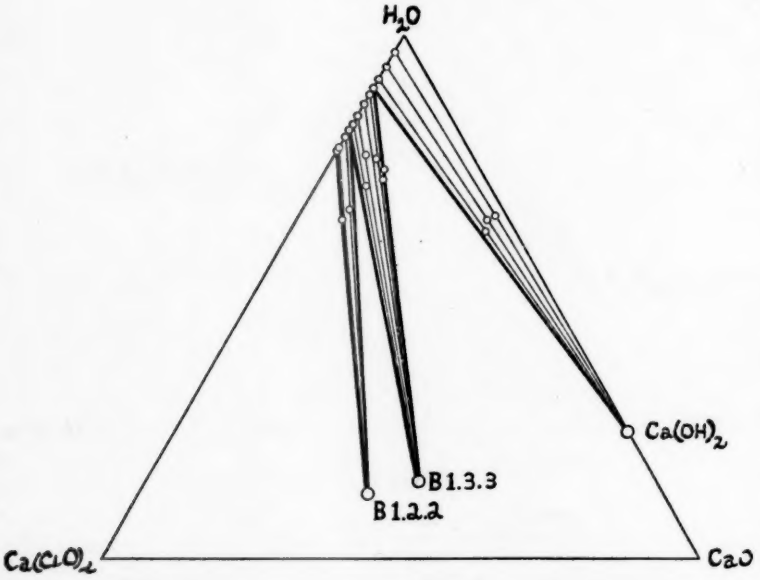
TABLE II.

	Composition, %.				
	Solution.		Residue.		
$d_4^{0°}$.	$Ca(ClO)_2$.	$CaCl_2$.	$Ca(ClO)_2$.	$CaCl_2$.	Solid phase.
1·213	21·8	—	—	—	
1·220	19·6	3·1	42·5	1·8	
1·228	18·6	5·3	40·2	3·1	
1·234	16·1	8·4	41·5	5·0	
1·238	14·0	10·8	38·9	6·7	
1·255	11·0	15·4	38·5	8·1	$Ca(ClO)_2,3H_2O$.
1·270	8·8	19·4	40·8	9·7	
1·285	7·4	22·2	37·8	12·1	
1·322	4·5	28·5	35·0	15·5	
1·333	4·2	30·7	35·2	16·4	
1·366	2·9	34·0	34·1	18·9	
1·388	2·6	36·4	—	—	$Ca(ClO)_2,3H_2O + CaCl_2,6H_2O$.
1·382	1·6	36·9	0·7	46·3	$CaCl_2,6H_2O$.
1·370	—	37·6	—	—	

E. *The System* $Ca(ClO)_2$–CaO–H_2O.—An extended series of measurements was undertaken, the procedure being in all cases

to add solid calcium hypochlorite to milk of lime, and to agitate the resulting complexes for periods varying from 1 to 5 days before analysis. In order to avoid the presence of lumps, freshly burned calcium oxide was slaked in boiling water. Since accurate adjustment of the inital compositions of the complexes was sometimes necessary, the percentage of anhydrous substance in the calcium hypochlorite was determined immediately before use. Two basic salts were found (see Table III and Fig. 3) of formulæ $Ca(ClO)_2,2CaO,2H_2O$ and $Ca(ClO)_2,3CaO,3H_2O$. These are referred to as B 1.2.2 and B 1.3.3, respectively.

FIG. 3.



The salt B 1.2.2 was formed in a few hours from complexes containing from 21·8% to about 16% of calcium hypochlorite, but subsequent investigation showed that its range of stable existence at 0° extends only from 21·8% to 18·0%. Prepared as described above, it was rather voluminous and not visibly crystalline. In consequence, residues containing B 1.2.2 consisted chiefly of solution, although an apparently good filtration had been achieved. Nevertheless, the residue method was quite capable of giving the composition of the solid phase with certainty. The range of stable existence of B 1.2.2 is probably greater above 0°, as it was observed that preparations of B 1.3.3 decomposed on being allowed to warm to room temperature, producing minute crystals. When the rise

TABLE III.

	Composition, %.				
	Solution.		Residue.		
$d_4^{0°}$.	$Ca(ClO)_2$.	CaO.	$Ca(ClO)_2$.	CaO.	Solid phase.
1·030	3·0	0·106	1·85	32·6	$Ca(OH)_2$.
1·053	5·7	0·105	3·5	31·9	
1·077	8·2	0·110	4·8	32·6	
* 1·103	11·0	0·114	12·7	31·2	Variable.
* 1·122	12·7	—	10·6	19·5	
* 1·133	14·0	0·111	13·4	35·0	
1·093	9·9	0·091	15·9	9·8	B 1.3.3.
1·104	11·1	0·093	16·9	10·5	
1·123	13·0	0·093	16·3	7·35	
1·142	15·1	0·077	17·6	5·2	
1·161	16·9	—	20·3	8·3	
1·168	17·8	—	19·2	3·7	
1·171	18·0	—	22·4	6·7	B 1.3.3 + B 1.2.2.
* 1·154	16·1	—	16·3	7·4	B 1.2.2.
* 1·172	17·7	0·105	21·4	6·8	
1·173	18·2	—	24·0	8·1	
1·189	19·2	0·113	25·3	7·9	
1·188	19·8	0·106	25·0	7·2	
1·203	21·2	0·106	27·3	7·7	
1·213	21·8	—	—	—	$Ca(ClO)_2,3H_2O$.

* Metastable equilibria.

of temperature was slow, these were larger, taking the form of thin plates, 1—2 mm. in diameter, of great transparency and high lustre, entirely free from the greenish-yellow tint of the normal hypochlorite. They were transformed once more into B 1.3.3 on cooling to 0°. An excellent separation of residue from solution was possible, and the subsequent analyses proved conclusively that the crystalline substance was B 1.2.2.

The compound B 1.3.3 was formed after a few hours when calcium hydroxide was agitated at 0° with a solution containing not less than 15% of hypochlorite. It is definitely different in appearance from B 1.2.2, excessively voluminous, and not visibly crystalline. In consequence, the compositions of solutions and corresponding residues were quite close together. A complex consisting of 50 c.c. of the above solution with about 1 g. of calcium hydroxide became of the consistency of cream, and larger amounts of calcium hydroxide produced a semi-solid mass—a fact which suggests that the basic salt may be highly hydrated; but all the evidence (see Fig. 3) is against this supposition. Over a range of solutions containing from 18·0% to 9·9% of calcium hypochlorite, the tie-lines converge fairly well upon the point representing B 1.3.3. They converge better on a point slightly to the right of this along a line joining the points representing B 1.3.3 and calcium hydroxide. This would indicate a basic salt of approximate composition B 2.7.7,

but the discrepancy may be due to experimental error or to the peculiarities of the system itself.

Introduction of a suspension of B 1.3.3. into preparations in which B 1.2.2 had been formed as solid phase revealed the metastable existence of the latter in contact with solutions containing from 18·0% to about 16% of hypochlorite, the change of solid phase occurring after a few hours' rotation. Owing to the relatively small quantities of calcium hydroxide which could be used, and the correspondingly small amounts of hypochlorite taken up in forming B 1.2.2 or B 1.3.3, it was not easy to obtain a residue containing both basic salts. This was finally produced by inoculating with B 1.3.3 a series of preparations which differed only very slightly from one another in initial composition, and in which B 1.2.2 had already been formed. The difference in appearance of the two basic salts confirmed the analytical results.

The equilibrium of B 1.3.3 and calcium hydroxide with solution could not be determined satisfactorily in spite of many attempts. The separation of B 1.3.3 did not always occur spontaneously when calcium hydroxide was agitated with solutions containing less than about 14% of calcium hypochlorite. Inoculation from another preparation caused it to separate, less and less readily, however, as the concentration of the solution fell. Below a concentration of 10% the appearance of the suspended solid and of the residues was entirely that of calcium hydroxide, even after inoculation and subsequent rotation for several days, but analysis revealed a small proportion of hypochlorite in the solid phase. The best available approximation to the conditions of the equilibrium in question was obtained as follows. About 40 c.c. of a solution containing some 13% of calcium hypochlorite in contact with 2·5 g. of calcium hydroxide were seeded with B 1.3.3 and rotated for several days. A large quantity of B 1.3.3 separated, but, owing probably to its slow formation, did not make the preparation unmanageable. The solution contained 9·9% hypochlorite, and the residue was practically free from hydroxide. Similar treatment of preparations in which the initial concentrations of the solutions varied from 12% to 10% yielded final solutions more concentrated than the above and residues of B 1.3.3 and calcium hydroxide. Reproducible results could not be obtained, and after a number of experiments the figure 9·9% was taken as a provisional lower limit to the range of stable existence of B 1.3.3 in contact with solution.

The concentration of calcium hydroxide in the solutions was small and its variation smaller, furnishing no guide to the establishment of equilibrium. In some cases, it was not determined.

When agitated with solutions containing from 14% to 10% of calcium hypochlorite, calcium hydroxide took up varying small quantities of hypochlorite, which increased with both the concentration of the solution and the time of agitation. Below 10%, the quantity was negligible. The appearance of the solid phase and residues was that of calcium hydroxide. This effect points to adsorption, mixed crystal formation, or production of some basic salt in variable amounts; but no decision between these possibilities could be made. Some of the analytical results are included in Table III, marked with an asterisk to indicate that they represent metastable conditions. Only equilibria believed to be stable are shown in Fig. 3.

Of the basic salts reported by the Chemische Fabrik Griesheim-Elektron (*loc. cit.*), only two (B 1.2.2 and B 1.3.3) have been found to exist at 0° in contact with solutions containing hypochlorite and hydroxide. There is no definite evidence at this temperature of any other basic salt.

Conclusions.

Although equilibria in the appropriate quaternary system have not been investigated, it is possible to discuss at the present stage the probable composition of bleaching powder. A fresh sample, prepared by chlorinating nearly dry calcium hydroxide and containing about 35% of available chlorine, is roughly of the composition $2Ca(ClO)_2 + 2CaCl_2 + 3Ca(OH)_2 + 4H_2O$. No compound of calcium hypochlorite and chloride exists at 0°, and the same is probably true at higher temperatures, as indicated by the method given for the preparation of the former salt. If present separately, the hypochlorite and chloride cannot be wholly in the form of trihydrate and hexahydrate, respectively, because the amount of water present is too small. Lower degrees of hydration, at least of the calcium chloride, are possible. Further, in ordinary good bleaching powder, the proportion of calcium hydroxide is too small to convert completely either the hypochlorite or the chloride present into any of the known basic salts, except $CaCl_2,CaO,2H_2O$. The extent to which these substances are present in dry bleaching powder prepared in the usual way is necessarily problematical, and is further limited in the case of $CaCl_2,3CaO,16H_2O$ by the amount of water available. The equilibrium distribution of the water and calcium hydroxide present, and the possibility of formation of a basic double salt cannot be discussed on the basis of the data at present available, but it appears likely that, in a solid preparation, basic salt formation, if it occurs at all, would be slow, and that fresh bleaching powder is therefore simply a mixture of calcium hydroxide with more or less hydrated hypochlorite and chloride.

Summary.

1. A method was developed for the isolation of relatively pure calcium hypochlorite.

2. The ternary systems $CaCl_2$–CaO–H_2O, $Ca(ClO)_2$–$CaCl_2$–H_2O, and $Ca(ClO)_2$–CaO–H_2O have been investigated at 0°.

3. Basic salts $CaCl_2,3CaO,16H_2O$; $Ca(ClO)_2,CaO,2H_2O$; and $Ca(ClO)_2,3CaO,3H_2O$ were identified.

4. No double salt was formed by calcium hypochlorite and calcium chloride.

5. The probable composition of bleaching powder has been discussed in the light of these results.

It is proposed to extend this investigation, and to attempt the isolation of the hypochlorites of metals other than calcium.

THE UNIVERSITY OF QUEENSLAND,
BRISBANE. [*Received, June 22nd,* 1927.]

CCCLIX.—*Some Effects of the Uneven Distribution of Current Density over an Electrode.*

By ERNEST SYDNEY HEDGES.

IN the ordinary course of electrolysis, the current density is not evenly distributed over a rectangular electrode, but tends to concentrate at the corners and edges. (Possibly, this is related to the well-known tendency of an electric charge to escape from a point.) Thus, whenever film formation takes place at such an electrode, the film first forms at the lowest part of the electrode and travels up the metal in the form of a U of diminishing concavity. This is not due to a concentration gradient in the solution, for the phenomenon occurs however vigorously the liquid is stirred, and is independent of the direction of flow of liquid over the electrode. For the same reason, the inside of an anode (*i.e.*, the side facing the cathode) is more readily attacked than the outside. At a cathode, more metal is deposited on the inside than on the outer side, and the deposit is thicker at the corners and edges.

In experiments with the easily passivated metals, some curious effects were observed through this behaviour. Anodes of iron were often found to be passive on the inside and active on the outside, where no oxygen was evolved; or, at somewhat higher *C.D.*'s, the lower portion of the outside of the electrode became passive, leaving the upper portion active, with the characteristic U-shaped boundary of separation. In certain cases, a small active

area was left near the liquid line, where rapid corrosion took place (compare Evans, J., 1927, 1035; Hedges, J., 1926, 831). It may be necessary to consider this factor in the type of liquid-line corrosion which is characterised by the presence of passivating media. In other cases, the main electrode remained active, whilst just the corners and edges of the electrode became passive. The most striking effects were observed with anodes of cobalt, which readily become passive, with evolution of oxygen, in moderately concentrated solutions of sulphuric acid. In 50% (by vol.) sulphuric acid cobalt dissolves at low *C.D.*'s as a pink, cobaltous ion, but at higher *C.D.*'s it goes into solution as a green cobaltic compound. It was frequently observed that the inside of the electrode was dissolving to give a green solution, whilst the outside dissolved simultaneously to form a red solution.

An interesting conclusion may be drawn from these observations in connexion with Adler's theory (*Z. physikal. Chem.*, 1912, **80**, 385) of the cause of the periodic anodic dissolution of passive metals, according to which the periodic phenomenon is to be traced to alternations of polarity in local elements composing the electrode. In the experiments described above, periodic phenomena were observed, but they did not consist of an alternation of the active and passive regions. The phenomena did not differ in any respect from those observed at higher *C.D.*'s, when the whole surface of the electrode became alternately active and passive. Moreover, electrodes have been observed which, although clearly differentiated into active and passive zones, did not dissolve periodically.

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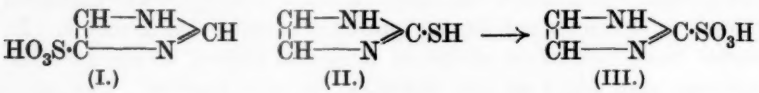
CCCLX.—*The Sulphonation of Glyoxalines. Part III.*

By GEORGE REGINALD BARNES AND FRANK LEE PYMAN.

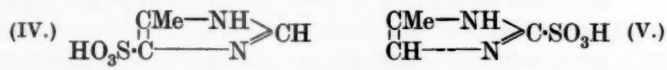
SULPHONATION of glyoxalines leads to a monosulphonic acid, which was assumed to be glyoxaline-4(5)-sulphonic acid (I) (Pyman and Ravald, J., 1920, **117**, 1429), but attempts to prove the orientation of the sulpho-group failed (Forsyth, Moore, and Pyman, J., 1924, **125**, 919). Recently, Balaban and King (this vol., p. 1858) have shown that 2-thiol-4(5)-methylglyoxaline can be oxidised to 4(5)-methylglyoxaline-2-sulphonic acid by means of hydrogen peroxide, and with the consent of these authors we have oxidised 2-thiol-glyoxaline (II) to *glyoxaline-2-sulphonic acid* (III) by their method. It proves to be different from the sulphonation product of glyoxaline,

which is thus shown to be glyoxaline-4(5)-sulphonic acid, as previously supposed.



(I.) (II.) (III.)

4(5)-Methylglyoxaline has now been sulphonated, and yields a sulphonic acid which must be 4(5)-*methylglyoxaline*-5(4)-*sulphonic acid* (IV), since it is not identical with Balaban and King's 4(5)-methylglyoxaline-2-sulphonic acid (V).



(IV.) (V.)

It resembles glyoxaline-4(5)-sulphonic acid and 2-methylglyoxaline-4(5)-sulphonic acid in being readily decomposed by cold bromine water and in failing to yield an acid chloride on treatment with phosphorus pentachloride. Like glyoxaline-4(5)-sulphonic acid, it is hydrolysed almost quantitatively by heating for 3 hours at 170° with concentrated hydrochloric acid, but glyoxaline-2-sulphonic acid is hydrolysed only to the extent of 12% under these conditions. It may be noted that all the many sulphonation and nitration products of glyoxalines which have been oriented hitherto contain the sulpho- or nitro-group in the 4- or 5-position, and there is no evidence at present that glyoxalines can be sulphonated or nitrated in the 2-position.

Experimental.

Glyoxaline-2-sulphonic Acid (III).—2-Thiolglyoxaline (3·21 g.) was added to Merck's perhydrol (10·92 g.) diluted with water (21·8 c.c.) at − 5° to 0°. The solution was basified with sodium hydroxide, kept at 0° for 12 hours, and acidified to Congo-red with hydrochloric acid. When the solution was concentrated, *glyoxaline-2-sulphonic acid* (2·46 g.; yield 46·2%) separated. The mother-liquor was basified with potassium carbonate, evaporated to dryness, and extracted with alcohol. This extract gave with picric acid glyoxaline picrate (0·8 g.; yield 8·4%).

Glyoxaline-2-sulphonic acid crystallises from water in colourless prisms containing $1H_2O$, which is lost in a vacuum over sulphuric acid. The dried acid softens and darkens from 285° and melts at about 303° (corr.), whilst a mixture of this acid with the monosulphonic acid formed by the sulphonation of glyoxaline—glyoxaline-4(5)-sulphonic acid, m. p. 307°—melted at 272—275°. (The latter crystallises from water in anhydrous cubes; Pyman and Ravald, *loc. cit.*) (Found: loss in a vacuum over H_2SO_4, 11·0, 11·1.

$C_3H_4O_3N_2S,H_2O$ requires H_2O, 10·8%. Found in dried acid: C, 24·3; H, 3·1; S, 21·7. $C_3H_4O_3N_2S$ requires C, 24·2; H, 2·7; S, 21·6%).

Glyoxaline-2-sulphonic acid is soluble in about 8 parts of cold water, more readily soluble in hot water, but insoluble in absolute alcohol.

The *barium* salt crystallises from water in feathery needles containing $2H_2O$, and is soluble in about 3 parts of cold water, more readily soluble in hot water, but insoluble in alcohol [Found: loss at 120°, 7·2. $(C_3H_3O_3N_2S)_2Ba,2H_2O$ requires H_2O, 7·7%. Found in dried salt: Ba, 31·3, 31·4. $(C_3H_3O_3N_2S)_2Ba$ requires Ba, 31·8%]. [Barium glyoxaline-4(5)-sulphonate crystallises from water in anhydrous octahedra; Pyman and Ravald, *loc. cit.*].

Hydrolysis. Glyoxaline-2-sulphonic acid (0·83 g.) and concentrated hydrochloric acid (8·3 c.c.) were heated for 3 hours at 170°, and the product was mixed with aqueous barium chloride; barium sulphate was then precipitated in quantity (0·14 g.) corresponding to the hydrolysis of 12% of the acid. After removal of the excess of barium by means of sulphuric acid, and of hydrochloric acid by means of silver hydroxide, 0·45 g. (54%) of glyoxaline-2-sulphonic acid was recovered unchanged, whilst the mother-liquor gave with picric acid glyoxaline picrate (0·1 g.; yield 6·7%). This melted at 205°, and did not depress the m. p. of an authentic specimen of glyoxaline picrate.

Sulphonation of 4(5)-*Methylglyoxaline.*—The well-dried and finely powdered sulphate from 16·76 g. of 4(5)-methylglyoxaline was added to 60—70% oleum (67·0 g.) at 0°, and the mixture heated for 6 hours at 160°. The product was diluted with water, and sulphuric acid removed by means of barium hydroxide, excess of the latter being removed by carbon dioxide. The filtered solution was evaporated to dryness, and the residue was extracted with chloroform, which removed no unchanged base, and dried at 120°; 43·44 g. of crude barium salt containing 29·2% Ba were then obtained. These figures correspond to a yield of 90·5% of barium 4(5)-methylglyoxaline-5(4)-sulphonate, but when the salt was treated with the calculated quantity of sulphuric acid pure 4(5)-methylglyoxaline-5(4)-sulphonic acid was obtained in only 60% yield, and was accompanied by small quantities of a by-product more sparingly soluble in water, which was not obtained in a pure state.

4(5)-*Methylglyoxaline*-5(4)-*sulphonic acid* (IV) crystallises from water in colourless, hexagonal plates containing $1H_2O$, which is lost at 100°. The dried acid melts at 278° (corr.) after sintering a few degrees lower. A mixture of this acid with a specimen of 4(5)-methylglyoxaline-2-sulphonic acid (m. p. 280°), for which we

are indebted to Dr. King, melted at 235—240° (Found in air-dried acid : loss at 100°, 9·8, 10·0. $C_4H_6O_3N_2S,H_2O$ requires H_2O, 10·0%. Found in dried acid : C, 29·5; H, 4·1; N, 17·4; S, 20·2. $C_4H_6O_3N_2S$ requires C, 29·6; H, 3·7; N, 17·4; S, 19·8%). The acid is soluble in about 4 parts of cold water, more readily soluble in hot water, but insoluble in alcohol or ether.

The *sodium* salt crystallises from water in long, silky needles, containing $3H_2O$, and is soluble in about 2·5 parts of cold water, but insoluble in alcohol (Found in air-dried salt : H_2O, 21·7, 21·6; Na, 9·5, 9·6. $C_4H_5O_3N_2SNa,3H_2O$ requires H_2O, 22·7; Na, 9·7%). The *ammonium* salt crystallises from water in anhydrous prisms which are soluble in about 4 parts of cold water but insoluble in alcohol (Found : N, 23·3. $C_4H_9O_3N_2S$ requires N, 23·4%). The *barium* salt crystallises from 50% aqueous alcohol in long, opaque needles, containing $3H_2O$. It is soluble in 2 parts of cold water, but insoluble in alcohol [Found in air-dried salt : loss at 120°, 10·2, 10·4. $(C_4H_5O_3N_2S)_2Ba,3H_2O$ requires H_2O, 10·5%. Found in dried salt : Ba, 29·3, 29·5. $(C_4H_5O_3N_2S)_2Ba$ requires Ba, 29·8%].

Hydrolysis. 4(5)-Methylglyoxaline-5(4)-sulphonic acid (0·9 g.) was heated with concentrated hydrochloric acid (10 c.c.) for 3 hours at 170°. The product was mixed with aqueous barium chloride and gave 1·166 g. of barium sulphate corresponding to the hydrolysis of 99·8% of the acid. The filtrate was basified with sodium carbonate, filtered from barium carbonate, and evaporated to dryness. On extraction of the residue with chloroform an oil was obtained which gave with alcoholic picric acid 4(5)-methylglyoxaline picrate (0·89 g.; yield 57%; m. p. 159—160°, alone or mixed with an authentic specimen).

Bromination. To the hydrated sulphonic acid (9·62 g.) in cold water (100 c.c.), bromine (1 mol.; 2·7 c.c.) was added, and the colour of this was immediately discharged. On concentrating the solution and, on occasions, adding alcohol, various crops of crystals were obtained from which the unchanged acid (5·22 g.) and ammonium bromide (1·5 g.) were isolated. The final mother-liquor contained 1·03 g. of sulphuric acid.

Anhydrous 4(5)-methylglyoxaline-5(4)-sulphonic acid did not appear to react with phosphorus pentachloride at 160°.

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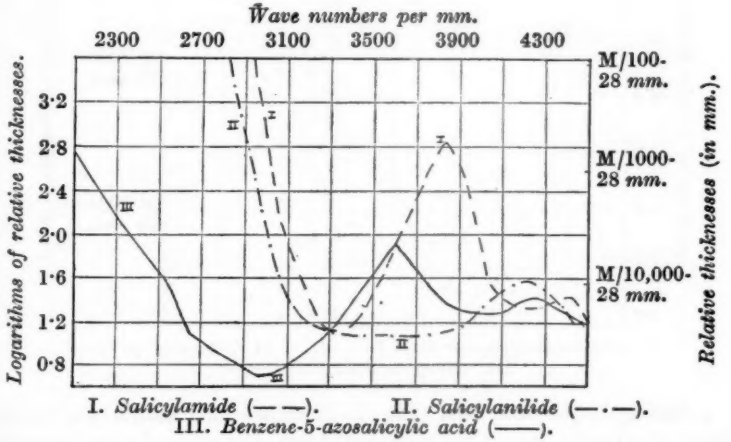
UNIVERSITY OF MANCHESTER. [*Received, October 5th*, 1927.]

CCCLXI.—*The Absorption Spectra of Various Alkaloids and their Salicylates and of other Derivatives of Salicylic Acid.*

By JOHN EDWARD PURVIS.

IN previous communications (J., 1925, **127**, 2771; 1926, 775; this vol., p. 780), the author has discussed the influence of the basic and acidic constituents of various salts on their absorption spectra. This communication is to describe the results of further investigations on the spectra of various alkaloids and their salicylates, and of other compounds derived from salicylic acid. The substances were dissolved in pure ethyl alcohol and a condensed cadmium spark was the source of radiant energy.

FIG. 1.



I. *Salicylamide* (— —). II. *Salicylanilide* (—·—).
III. *Benzene-5-azosalicylic acid* (——).

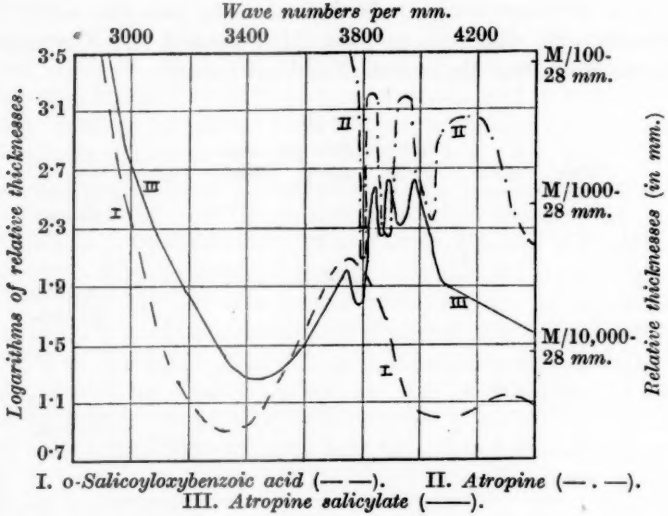
Salicylamide (Fig. 1, I) shows two bands. They are not unlike those of salicylic acid, but the more refrangible one is not quite so well marked as that of the acid. Hartley and Hedley (J., 1907, **91**, 319) found that the bands of benzamide and benzoic acid were comparable, except that the benzamide band was not so wide as that of the acid.

Salicylanilide has one large band (Fig. 1, II). Aniline itself has two large bands, namely, between $1/\lambda$ 3508 and $1/\lambda$ 3648 and between $1/\lambda$ 4165 and $1/\lambda$ 4309, as described by Hartley and Huntingdon (*Phil. Trans.*, 1879, **170**, 257) and by Baly and his colleagues (J., 1905, **87**, 1332; 1915, **107**, 1058). In salicylanilide, therefore, the two bands of aniline and the two bands of salicylic acid have been fused into one large band which covers the positions formerly

occupied by the bands of aniline and salicylic acid. These results are comparable with those obtained with benzanilide, where the bands of benzene and of aniline are replaced by one large band (Crymble, Stewart, Wright, and Glendinning, J., 1911, **99**, 451).

Benzene-5-azosalicylic acid shows two bands (Fig. 1, III). The absorption of the less refrangible and very wide one extends into the coloured regions, the group $C_6H_5\cdot N{:}N\cdot$ probably accounting for the colour. The more refrangible band is weaker than the corresponding band of salicylic acid and almost disappears.

FIG. 2.



I. o-*Salicoyloxybenzoic acid* (— —). II. *Atropine* (— . —).
III. *Atropine salicylate* (——).

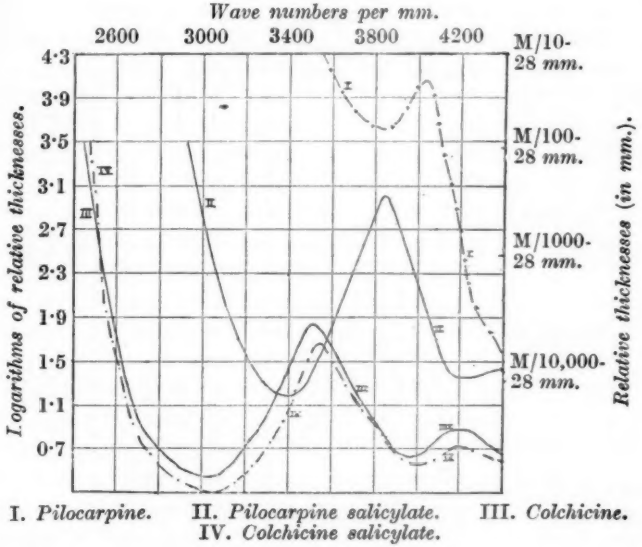
o-*Salicoyloxybenzoic acid* (Fig. 2, I) shows two bands not unlike those of salicylic acid in their general form, but shifted more towards the red end. It has been noticed (*loc. cit.*) that when the hydrogen of the hydroxyl group of salicylic acid is replaced by an acetyl group, as in *o*-acetoxybenzoic acid and other similar compounds, a striking change is produced and the absorption phenomena are not unlike those of benzoic acid. In *o*-salicoyloxybenzoic acid there is no such change, so that the presence of hydrogen of the hydroxyl group of $OH\cdot C_6H_4\cdot CO\cdot$ combined with the other group $-O\cdot C_6H_4\cdot CO_2H$ to produce the acid $OH\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$ enables the compound to retain the characteristic absorption of salicylic acid itself.

Atropine and Atropine Salicylate.—Dobbie and Fox (J., 1913, **103**, 1193) describe two bands of atropine at about $1/\lambda$ 3770 and $1/\lambda$ 3880. Gompel and Henri (*Compt. rend.*, 1913, **156**, 1541) found a third, weaker, band at $1/\lambda$ 4020. The author has repeated

these experiments and can confirm the presence of three bands (Fig. 2, II).

The curve of atropine salicylate (Fig. 2, III) exhibits a large band like that of salicylic acid, but not quite so strong. Besides that, there are three weak bands on the more refrangible side of this large band, and these are comparable with the three bands of atropine, but a little weaker. The more refrangible band of the acid is represented in the salt by a rapid extension of the rays between about $1/\lambda$ 4100 and $1/\lambda$ 4450. It is obvious, therefore, that the bands of both base and acid are still well marked in the

FIG. 3.



I. *Pilocarpine.* II. *Pilocarpine salicylate.* III. *Colchicine.* IV. *Colchicine salicylate.*

salt, the chief differences being the weaker appearances of the bands of the latter. A sharper differentiation of the separate bands of the basic and acidic parts of the salt could only be made by an instrument of much greater dispersion. This remark applies to the following observations of other alkaloids and their salts.

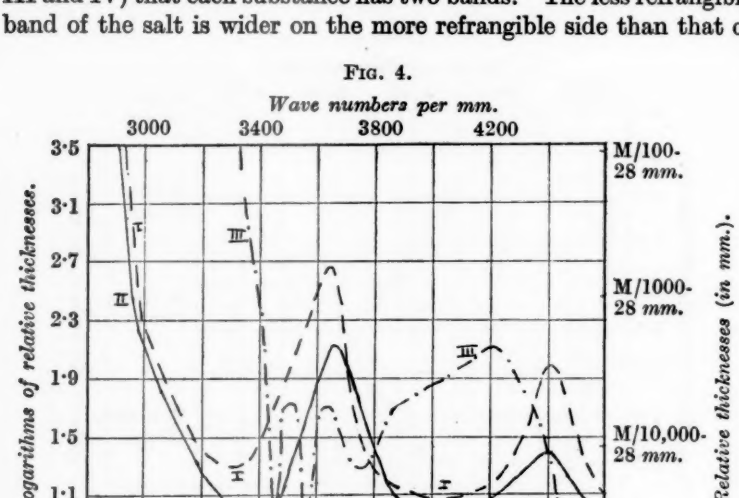
Pilocarpine and Pilocarpine Salicylate.—In Jowett's investigation of pilocarpine (J., 1903, **83**, 438), Dobbie describes a weak band of pilocarpine nitrate at about $1/\lambda$ 3350. The author has repeated the observations with an alcoholic solution of the base itself and finds a weak band at about $1/\lambda$ 3800 (Fig. 3, I).

Pilocarpine salicylate shows two bands of salicylic acid (Fig. 3, II). As the thickness of the solution increases, the less refrangible band of the salt appears to be slightly wider than that of the acid; and

this is probably caused by the latter impinging on the weak band of the base and covering it up; the absorptive power of the base only becomes visible as the thickness of the solution increases. A saturated solution of pilocarpine salicylate was also examined, but there was no appearance of a separate band of pilocarpine, showing that the bands of the acidic constituent covered up that of the basic part. The more refrangible band of the salt is not so well marked as that of the acid itself.

Colchicine and Colchicine Salicylate.—The curves show (Fig. 3, III and IV) that each substance has two bands. The less refrangible band of the salt is wider on the more refrangible side than that of

FIG. 4.



I. *Eserine* (— —). II. *Eserine salicylate* (——). III. *Indole* (— . —).

the base, and the more refrangible band of the base is stronger than the more refrangible one of the salt. These differences are probably again caused by the overlapping of the separate bands of the basic and acidic constituents. A greater dispersion would be necessary to separate these bands more sharply. The general shift of the absorption towards the red end explains the slight yellow colour of both these substances.

Eserine (*Physostigmine*) *and Eserine Salicylate.*—The absorption curves (Fig. 4, I and II) show that each substance has two large bands, and, as in colchicine and its salicylate, the differences are the result of the bands of the acid and basic constituents partly overlapping each other. It was suggested by Stedman and Barger and experimentally confirmed by Späth and Brunner (*Ber.*, 1925, 58, 518) that physostigmine is a substituted indoline. The author

has investigated the absorption of indole and the curve is compared with that of eserine (Fig. 4, III). This exhibits several bands at $1/\lambda$ 3460, $1/\lambda$ 3560, and a weaker wider one at $1/\lambda$ 3750. There is also a rapid extension of the line of absorption to about $1/\lambda$ 4200, and this probably indicates other weaker bands. All the bands of indole disappear in eserine.

These results are to be compared with those described in the previous investigations (*loc. cit.*). In camphor salicylate, for example, the weak band of camphor at $1/\lambda$ 3480 would appear to be covered up by the less refrangible strong band of salicylic acid, which widens out with increased thickness of the solution, to $1/\lambda$ 3600. Camphor salicylate has again been studied in $M/10$-solutions, and these are stronger than those of the earlier observations, and through thicknesses of from 2 mm. to 28 mm. No camphor band appeared, whereas in camphor itself the band is perfectly clear in such strengths. Similar explanations account for the differences in theobromine and caffeine and their salicylates (*loc. cit.*). In the salicylates of phenazone and quinine (*loc. cit.*), the differences in the absorption are more clearly marked because the specific bands of the bases themselves are fairly strong, and they are not hidden by the bands of the acid nuclei.

The specific absorptive capacity of these compounds, therefore, appears to depend upon the more or less intimate chemical combination of the various centres, as well as upon their chemical type. Where the chemical combination is not so close, as in the salicylates of the alkaloids, both the basic and the acid nuclei largely retain their own specific absorption. On the other hand, where there is a closer chemical combination of the absorbing centres, as, for example, in salicylanilide or benzene-5-azosalicylic acid, the specific absorption of each centre is not so sharply defined. Each centre is influenced by the other centres to a much larger extent than in the salicylates of the alkaloids and other organic bases.

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CCCLXII.—*Organic Derivatives of Silicon. Part XXXIII. An Amorphous Variety of Octaphenylcyclosilicotetrane.*

By FREDERIC STANLEY KIPPING.

THE glue-like, readily soluble product (E) of the action of sodium on diphenylsilicon dichloride in toluene solution is so strikingly different in physical properties from the four very sparingly soluble

silicohydrocarbons $[SiPh_2]_n$ (A, B, C, and D) by which it is accompanied (Kipping and Sands, J., 1921, **119**, 830) that it could hardly fail to arouse interest; its investigation, continued intermittently since 1921, has led to the conclusion that it consists mainly of an amorphous form of octaphenyl*cyclo*silicotetrane (B), the crystalline variety of which does not melt at 400° and is practically insoluble in cold acetone.

The acetone solution of (E) (*loc. cit.*, p. 836), kept in a closed vessel, continues to deposit crystals, but in gradually diminishing quantities, over periods of more than two years; these deposits consist of octaphenyl*cyclo*silicotetrane (B), but contain, as a rule, a very small proportion of the compound (C) (Kipping, J., 1924, **125**, 2291); octaphenylsilicotetrane (A), which is much more soluble than (C), but much less soluble than (B), in ordinary media, has never been detected. It seems, therefore, that (E) is partly and very slowly transformed into (B), since ordinary supersaturation could hardly continue so long. When the acetone solution is systematically fractionally precipitated with alcohol, a very small proportion of (B) and sometimes traces of (C) are found after each extended set of operations, and this separation or formation of insoluble matter seems to continue almost indefinitely; most of the original preparation, however, is merely resolved into a series of fractions, all miscible with acetone, the more sparingly soluble of which consist of an easily fusible resinous material of the composition $[SiPh_2]_n$, hereafter referred to as (E_1). The more soluble fractions are glue-like or oily, and contain combined oxygen, the origin of which was ultimately traced to the presence of phenoxy- and ethoxy-compounds in the diphenylsilicon dichloride (compare Kipping and Murray, this vol., p. 2734). This discovery and the difficulty of settling the nature of (E_1) made it advisable to hold back the results of its investigation until there was no doubt of its formation from the dichloride.

Even after prolonged fractionation from many different solvents, (E_1) yields no crystalline compound, other than a little (B) and traces of (C); it merely affords a series of graded fractions. Cryoscopic determinations in benzene solution give multiples of $SiPh_2$ ranging from about 7 to 9, and the high molecular complexity of the material is also proved by its non-volatility at high temperatures in a vacuum (p. 2725).

In chemical behaviour, (E_1) resembles octaphenyl*cyclo*silicotetrane (B) and is quite different from the reactive, open-chain isomeride (A); the fact that it does not combine with iodine seems to indicate, but does not prove [compare behaviour of (D), J., 1924, **125**, 2296], that it consists entirely of closed-chain molecules. It

is oxidised by nitric acid, giving a small proportion of the rhomboidal oxide, $Si_4Ph_8O_2$ (J., 1921, **119**, 844), but practically the whole of it seems to be converted into diphenylsilicanediol and condensation products of the latter. It is decomposed by piperidine and aqueous alkali, giving hydrogen and diphenylsilicanediol (or condensation products). The observed hydrogen values (Kipping and Sands, *loc. cit.*, p. 848) are a little lower than that required for $SiPh_2 + 2H_2O = SiPh_2(OH)_2 + H_2$, probably owing to incomplete hydrolysis; the examination of the products (p. 2727) seems to prove, however, that the preparations do not contain any $SiPh_3$-groups, but consist entirely of molecules $[SiPh_2]_n$.

Now when the physical properties of (E_1) are compared with those of octaphenyl*cyclo*silicotetrane (B) and those of (C), which is possibly $[SiPh_2]_6$ or $[SiPh_2]_8$—leaving out of consideration those of the open-chain compounds (A) and (D)—the contrast is so striking that even if (E_1) were regarded as a mixture of several cyclic compounds $[SiPh_2]_n$, the latter could hardly be present as free molecules, capable of forming sparingly soluble crystalline structures of high melting point, like those of (B) and (C). It is therefore suggested that (E_1) consists of molecules of octaphenyl*cyclo*silicotetrane (B) which have got so entangled with one another during their formation that they are inseparable, or nearly so, by physical means at moderate temperatures. It is not assumed that the cyclic structures are joined together like the links of a chain, but that the molecules of (B) are held together by the interlocking of their phenyl groups, forming aggregates of irregular shape, which do not themselves pack into crystals and hinder the orderly arrangement of the whole; if some of these molecules were comparatively loosely attached, and the proportion of irregular aggregates was diminished, a slow deposition of ordinary crystals of (B) from solutions of (E_1) might be expected to take place to a certain extent, as actually occurs. It is possible that octaphenyl*cyclo*silicotetrane and its higher analogues might assume configurations in which the silicon atoms do not all lie in one plane, and that such configurations might be rendered stable by the steric effects of their phenyl groups. Such assumptions, however, would not account adequately for the properties of (E_1), which seems to be a complex mixture of molecules, incapable of crystallisation.

The view that (E_1) is merely a physically different form of (B) is borne out by the following: In one experiment, when (E) was heated under 5—0 mm., small quantities of oily "distillate," apparently decomposition products, were collected as the temperature of the liquid rose from about 300° to 400° and at the same time a very considerable proportion of crystalline matter separated

from the residue, and did not all redissolve; this crystalline deposit consisted of octaphenyl*cyclo*silicotetrane (B) with a small proportion of octaphenylsilicotetrane (A). As it was hardly possible that so large a proportion of free (B) molecules could have been present in the crude (E), it must be concluded that these molecules had been set free by the action of heat.

Unfortunately, attempts to repeat this conversion of (E_1) into (B) have been unsuccessful, but the reverse operation is easily accomplished. When pure (B) is very rapidly heated above 400° until it is partly melted, and then immediately cooled, the glue-like melted portion is very readily soluble in cold acetone; the solution begins to deposit crystals of (B) after a variable interval and continues to do so during several days or weeks; it then gives with alcohol a flocculent precipitate, $[SiPh_2]_n$, melting indefinitely below 150°, and having a molecular weight of about 1500.

These results, the chemical similarity of (E_1) and (B), and all other facts seem to be best accounted for by the assumption that these two substances are physically different forms of octaphenyl-*cyclo*silicotetrane.

The distillate referred to above, and a similar product from other samples of (E), consisted mainly of an oil which gave triphenylsilicol on oxidation, or, with evolution of hydrogen, on treatment with acetone and alkali; from these facts, it would appear that this oil contained triphenylsilicyl, pentaphenylsilicoethyl, or heptaphenylsilicopropyl. It is only formed from (E) very slowly and at high temperatures, but it is clear that the decomposition of the $[SiPh_2]_n$ molecules is accompanied by a transference of phenyl groups from one silicon atom to another.

Experimental.

The crystalline deposit which is formed when an acetone or ethereal solution of (E) is kept in a closed vessel does not redissolve when the supernatant solution is warmed; separated by filtration and treated with cold benzene, it often leaves a very small proportion of a residue which can be identified as (C) by crystallisation from benzene, etc. (compare J., 1924, 125, 2294). The main portion of the deposit, soluble in cold benzene, was identified as octaphenyl*cyclo*silicotetrane (B) by direct comparison; it did not decolorise a very dilute benzene solution of iodine and was therefore free from octaphenylsilicotetrane (A).

As the formation of deposits in acetone solutions of (E) might conceivably be due to the action of alkali from the glass vessels, an acetone solution which had been kept some 3 months was filtered and acidified with a drop of hydrochloric acid; the solution (in a

closed vessel, gave in the course of 6 months a deposit of (B), and the flask became coated with a very thin layer of some material insoluble in boiling benzene and other solvents, which could be detached in transparent, elastic films. Similar gelatinous films are often formed on the beakers used in fractionating (E) with acetone and alcohol; they char at a very high temperature but without melting and appear to be unchanged when boiled with acetone and potash. This material may be already contained in (E) and if so may be partly accountable for the low hydrogen values of (E_1), or it may be a very complex condensation product of diphenylsilicanediol (which will be described in a future paper), produced by the hydrolysis of (E_1). Crude (E) does not react appreciably with iodine, but it reduces silver nitrate in acetone solution very distinctly.

Separation of Silicohydrocarbons (E_1).—Treated with alcohol, the acetone solution of (E) gives at first a white, plastic precipitate which can be pulled out into long, silk-like threads; the latter change into a very brittle solid when the solvents evaporate. By systematic fractional precipitation in this way, or with water, continued until each of the original fractions (say 8) has been redissolved and reprecipitated several times, the most sparingly soluble portion, now precipitated in a flocculent form, if again treated with cold acetone, usually gives a very small separation of (B) with traces of (C). Another systematic series of operations with the whole set of fractions, starting from the most soluble portion, yields a similar result, and it seems that this very sparingly soluble matter is being continually produced.

Many different preparations of the less soluble fractions (but miscible with acetone) have been analysed; most of them retained solvent very tenaciously and lost in weight during more than 30 days in a vacuum * (Found: Si, 15·3, 15·7, 15·5, 15·6, 15·4, 15·6; C, 77·6, 78·2, 77·9, 78·3; H, 5·9, 5·8, 5·9, 5·8; *M*, cryoscopic in benzene, 1558, 1395, 1456, 1225, 1410; hydrogen values, 110, 108, 113, 116. $SiPh_2$ requires Si, 15·5; C, 79·0; H, 5·5%; *M*, 182; hydrogen value, 122) (compare J., 1921, **119**, 848).

The somewhat low combustion results are partly due to the difficulty of burning the last traces of carbon in the silica residue;

* The best way of obtaining a sample ready for analysis is to dissolve it (2—3 g.) in a very little dry ether in a 300 c.c. beaker, evaporate the solvent on the water-bath to a "glue," and then, while the "glue" is still warm, evaporate the rest of the solvent quickly under reduced pressure; the residue froths and fills the beaker with a white foam, which after 10—15 minutes becomes ery brittle and can be easily broken up. Even such preparations do not become constant in weight in less than 3 to 5 days in a vacuum; to the unaided eye they appear to be beautifully crystalline.

the silicon determinations are trustworthy, since the residue obtained on ignition with sulphuric acid containing a little nitric acid is colourless.* The low hydrogen values have not been accounted for satisfactorily; they are partly due to the presence of some non-hydrolysable matter, possibly an amorphous form of (C).

When (E) has been prepared from diphenylsilicon dichloride of about 95—97% purity (compare Kipping and Murray, *loc. cit.*),† the product after two precipitations contains about 15·1% of silicon, consists mainly of (E_1), and does not give phenol on hydrolysis; the isolation of (E_1) then presents no very great difficulty. The earlier crude preparations of (E), however, contained only 12·5—14% of silicon, and the isolation of (E_1) required a prolonged series of fractional precipitations whereby a large proportion of rather more soluble glue-like matter was gradually separated; this material gave phenol and ethyl alcohol on hydrolysis.

The Silicohydrocarbon (E_1).—Many preparations of the composition $[SiPh_2]_n$ were fractionally extracted with boiling alcohol or boiling light petroleum, precipitated from hot phenol with alcohol, etc., but their properties underwent but little change, and no crystalline product, except perhaps traces of (B), could be isolated. The fractional diffusion of an acetone solution through unglazed earthenware also failed to afford crystals.

The preparations have no definite melting point but gradually liquefy over a range of 20° or 30° or so, beginning to sinter from about 110° to 130°; they are miscible with cold ether, benzene, chloroform and many other solvents, from all of which they separate as "glues," which very gradually become brittle, but they are only sparingly soluble in boiling light petroleum and very sparingly in boiling alcohol or glacial acetic acid. Preparations kept in the solid state during 4—5 years are still miscible with cold acetone.

(E_1) does not react appreciably with iodine in cold benzene

* The silica is very hygroscopic and may absorb as much as 28·4% of water on exposure to the air.

† It is no easy matter to ascertain whether—or when—the reaction with sodium is at an end. The toluene solutions of the product, which give no sign of a green flame with copper, afford an aqueous extract containing halogen. This seems to be partly present as sodium chloride, which is slightly soluble in toluene solutions of (E). The heating was usually stopped when an aqueous extract gave a neutral reaction to litmus, but even this test seems to be untrustworthy, and (E) may still contain halogen. If the heating with sodium is continued beyond a certain point, the filtered toluene solution gives an alkaline reaction, and the crude (E), obtained by evaporation, effervesces when treated with (undried) acetone; if this occurs, the fractional precipitation of the acetone solution with alcohol (after removing B) yields a large proportion of trianhydrotrisdiphenylsilicanediol, and the isolation of (E_1) is difficult or impossible.

solution; in carbon tetrachloride solution, a little bromine is absorbed, but many hours elapse before the proportion reaches $Br_2 : [SiPh_2]_2$. In some cases traces of a crystalline bromo-compound were obtained, but the principal solid product was a very little rhomboidal oxide, probably formed by the hydrolysis of a dibromide, $SiPh_2Br{\cdot}SiPh_2Br$, and subsequent condensation of the diol; the reaction seemed also to involve the partial separation of phenyl groups as bromobenzene without precipitation of silica.

When (E_1), partly dissolved and partly suspended in glacial acetic acid, is cautiously oxidised with nitric acid, it yields the rhomboidal oxide, but is almost entirely converted into crystalline and oily condensation products of diphenylsilicanediol.

Formation of (*B*) *and* (*A*) *from* (*E*).—A solution of (E) (30—35 g.) in undried commercial ether, which had been kept about 3 weeks in a closed vessel and then filtered from the deposit of (B), was evaporated and the residue heated in a very short-necked (2″) flask under 6 mm. pressure. At first a little (0·2 g.) diphenyl came over; the temperature then rose rapidly to about 300° (thermometer in liquid) and a very slow "distillation" commenced, fractions, each of about 1½ c.c., being collected at 300—330°, 330—350° and 350—360°. The temperature then rose slowly to 400° (5 mm.), but no further distillation occurred and crystals which had been splashed on to the sides of the flask had not liquefied when the heating was stopped.

When cold, the glue-like mass was treated with acetone and left over-night; most of it dissolved, leaving some crystalline matter (about 2 g.), which was washed with acetone. This product was almost completely soluble in cold chloroform, and was reprecipitated by acetone in short, rectangular prisms which were identified as those of octaphenyl*cyclo*silicotetrane (B) by a direct comparison. The portion insoluble in cold chloroform (about 0·1 g.) crystallised from benzene in short, flat prisms and was proved to be octaphenylsilicotetrane (A) by its behaviour towards iodine and in other ways.

In order to prove that the cyclic silicohydrocarbon (B) had not been held in solution by the liquid "distillate" of (E), some of it was dissolved in a portion of this distillate; the solution, diluted with ether or with acetone, gave an immediate precipitate and apparently the whole of the dissolved (B) was deposited.

Of the three fractions referred to above, the two more volatile ones fumed very slightly in the air and contained halogen.* All three fractions deposited traces of trianhydrotrisdiphenylsilicanediol, reduced an aqueous solution of silver nitrate in a marked manner, and gave hydrogen very readily with acetone and aqueous

* The heating with sodium had been continued during at least 6 hours.

alkali. The whole of this thick, oily " distillate " was poured into glacial acetic acid (about 4 vols.)—in which it was only very sparingly soluble—and then a few drops of concentrated nitric acid were added; oxidation set in very readily and after the non-homogeneous mixture had been warmed on the water-bath during some 2 hours and then cooled, a considerable quantity of crystalline matter separated very slowly from the oily layer. This crystalline product, purified by recrystallisation from alcoholic chloroform, was conclusively proved to be triphenylsilicol by analysis, mixed melting-point determinations, etc., and by converting it into triphenylsilicyl oxide (m. p. 222—223°).

The fact that this oil gave a large proportion (at least 25%) of triphenylsilicol on oxidation, whereas undistilled (E) gives no such product, seemed to prove that a migration of phenyl groups had occurred without separation of silicon or silica. The acetone solution of the residue from the distillation, fractionally treated with alcohol, gave precipitates of much the same character as (E_1); they were, however, less readily soluble in acetone, and contained 16—17% of silicon ($SiPh_2$ requires 15·4%), the percentage increasing with the duration of the " distillation."

In the hope of confirming these results, another preparation of (E), which had been kept in dry ethereal solution during 19 days, was separated from the usual deposit, and the crude (E) (12 g.) obtained on evaporation of the solvent was heated under 1—1·5 mm. (thermometer in the liquid) in a very short-necked flask. From about 283° to 310°, about 1½ c.c. of a thick oil very slowly collected in the receiver, but there was no separation of crystals from the distillate or from the residue, even when the latter was treated with acetone.

The distillate contained only traces of halogen, reduced an aqueous acetone solution of silver nitrate, and gave triphenylsilicol on oxidation with a glacial acetic acid solution of nitric acid; when treated with alkali in acetone solution, it gave hydrogen readily at the ordinary temperature, and, after some of the solvent had been expelled, crystals of triphenylsilicol were deposited; these, left on porous earthenware, without having been freed from alkali, passed into crystals of the silicyl oxide. The mother-liquor from the silicol, warmed again with alcohol and alkali, gave further deposits of triphenylsilicyl oxide, and finally at least 80% of a portion of the original distillate was transformed into this compound.

All attempts to isolate triphenylsilicol or the oxide from other portions of this distillate without using nitric acid or alkali were unsuccessful; the oil certainly did not contain the oxide, nor did it give any crystals of the latter after it had been heated for a long

time with alcohol and hydrochloric acid. The residue from this "distillation" solidified to a very brittle resin, which behaved on hydrolysis quite differently from ordinary samples of (E), inasmuch as it gave, in addition to diphenylsilicanediol, a considerable proportion of triphenylsilicyl oxide. A direct comparison of two samples of the same preparation of (E), one of which had been heated at about 350° for some time, proved that only the latter gave triphenylsilicyl oxide on hydrolysis; from 3·7 g. of the unheated material, only about 0·25 g. was not ultimately convertible into diphenylsilicanediol or other products soluble in aqueous alkali.

It must be concluded from these results that at high temperatures some of the molecules composed entirely of $SiPh_2$ groups are decomposed, giving triphenylsilicyl, $SiPh_3$·, or some other compound containing a $SiPh_3$-group.

Conversion of Octaphenylcyclosilicotetrane into an Amorphous Form.—When pure (B) is very rapidly heated in a test-tube over a free flame in an inert atmosphere, it can be partly melted, and when the cooled product is treated with cold acetone, the melted portion dissolves, leaving the crystalline matter; by repeating these operations, the whole of any sample of (B) can be obtained in solution in about 1—2% of the volume of solvent which would have been required to dissolve the crystals, but not more than 0·1 g. of (B) should be heated at a time. The acetone solution begins to deposit crystals of pure (B) either within a few minutes or only after some hours, and this deposition may continue during many days: the filtered solution gives with alcohol an apparently amorphous, flocculent precipitate, which, when separated and freed from solvent, melts very indefinitely from 110° to 150° and contains 15·4% of silicon ($SiPh_2$ requires Si, 15·5%); the molecular weight in camphor was found to be 1500, whereas under the same conditions crystalline (B) gives the normal results for $[SiPh_2]_4$ (J., 1924, **125**, 2291). The alcoholic acetone filtrate from the amorphous precipitate gives on evaporation a little more of an apparently identical product.

As there is no charring, or evolution of vapour, or separation of insoluble matter when (B) is thus heated, and as the whole of the product seems to be silicohydrocarbon $[SiPh_2]_n$, it is concluded that the soluble amorphous product is merely a form of octaphenyl-*cyclo*silicotetrane in which the molecules have become entangled with one another. It is not suggested that this form, produced by melting (B), is identical with (E_1); it seems to differ from (E_1) in being more readily and more completely transformed into the crystalline variety, and may be regarded rather as a mixture of (B) molecules analogous to that which is contained in the original

toluene solution of (E) and from which a considerable proportion of (B) is rapidly precipitated on the addition of acetone.

The author has been assisted in this investigation by J. E. Sands and R. Vyle, M.Sc., and has also received financial help for the purchase of diphenylsilicon dichloride (kindly supplied by Boots' Pure Drug Company) from the Government Grant Committee of the Royal Society : for all such assistance he wishes to record his indebtedness.

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CCCLXIII.—*Organic Derivatives of Silicon. Part XXXIV. The Action of Sodium on Phenoxydiphenylsilicyl Chloride.*

By FREDERIC STANLEY KIPPING.

SINCE the product (E) of the action of sodium on diphenylsilicon dichloride may give on hydrolysis appreciable quantities of phenol (this vol., p. 2724), it was inferred that the dichloride, in spite of its constant boiling point, might be contaminated with phenoxyphenylsilicon dichloride, phenoxydiphenylsilicyl chloride, or diphenoxydiphenylsilicane. It is known that atmospheric oxidation may occur during the preparation of magnesium phenyl bromide (Porter and Steel, *J. Amer. Chem. Soc.*, 1920, **42**, 2650) and the resulting Grignard reagent, containing magnesium phenoxy-bromide, might give rise to phenoxy-derivatives if used for the preparation of diphenylsilicon dichloride from silicon tetrachloride.

The action of phenol on diphenylsilicon dichloride was therefore studied, partly in order to observe the boiling points of two of the phenoxy-derivatives just mentioned, but mainly in the hope that by the fractional distillation of the product some other unknown impurity in the dichloride might be isolated and identified.

The results gave no support to the inference that the dichloride formed a constant-boiling mixture with either of these phenoxy-derivatives, and the product—consisting of phenoxydiphenylsilicyl chloride, diphenoxydiphenylsilicane, and unchanged diphenylsilicon dichloride—could be separated into its components by fractional distillation; no fraction representing the long sought-for impurity in the dichloride (compare Kipping and Murray, this vol., p. 2734) was obtained.

The action of sodium on phenoxydiphenylsilicyl chloride was then examined in the hope that symmetrical diphenoxytetraphenyl-

silicoethane would be produced, just as hexaphenylsilicoethane is formed from triphenylsilicyl chloride (Kipping, P., 1911, **27**, 144); the results were quite unforeseen. The products, isolated with the aid of anhydrous solvents, were octaphenylsilicotetrane,

$$-SiPh_2\cdot SiPh_2\cdot SiPh_2\cdot SiPh_2-$$

(Kipping and Sands, J., 1921, **119**, 830; Kipping, J., 1923, **123**, 2590), diphenoxyoctaphenylsilicotetrane, $PhO\cdot[SiPh_2]_4\cdot OPh$, and diphenoxydiphenylsilicane; from the remaining material, with the use of other solvents not free from water, phenol, diphenylsilanediol, a considerable proportion of an apparently amorphous solid, which is possibly $PhO\cdot[SiPh_2]_4\cdot OH$, and a very viscous oil, possibly $PhO\cdot SiPh_2\cdot SiPh_2\cdot OPh$, were obtained.

The formation of octaphenylsilicotetrane suggested that the phenoxy-chloride was contaminated with diphenylsilicon dichloride; but in subsequent preparations, using only material which, from its boiling point and from analyses, was the pure phenoxy-derivative, the three products named above were again obtained, apparently in the same yields as before; moreover, that of the silicohydrocarbon seemed to be about as large as if diphenylsilicon dichloride had been used instead of the phenoxy-chloride.

Now the supposed phenoxy-chloride cannot be a mixture of equal quantities of diphenylsilicon dichloride and diphenoxydiphenylsilicane. The product of the action of phenol (1 mol.) on the dichloride is not a liquid of constant boiling point, but distils over a range of about 100°. Further, the phenoxy-chloride is immediately and completely soluble in a cold 5% solution of potassium hydroxide, whereas the diphenoxy-derivative is practically insoluble in, and is only slowly hydrolysed by, such a solution; a prepared solution of the diphenoxy-compound in the dichloride gives crystals of the former when it is added to cold aqueous alkali. Another important fact, which seems to show that the phenoxy-chloride is not converted into a mixture of the dichloride and the diphenoxy-derivative at any stage of the reaction, is that, so far as can be ascertained, the other products of the action of sodium on diphenylsilicon dichloride, namely, octaphenyl*cyclo*silicotetrane (B) and the complex silicohydrocarbons (C) and (D) (Kipping, J., 1924, **125**, 2291), are not formed from the phenoxy-chloride. Finally, the production of diphenoxyoctaphenylsilicotetrane proves that a phenoxy-derivative takes part in the reaction, but apparently diphenoxydiphenylsilicane is not attacked by sodium even at temperatures above 110°.

Although, therefore, it must be concluded that octaphenylsilicotetrane and its diphenoxy-derivative are obtained from the phenoxy-chloride, the mechanism of their formation is obscure. The pro-

duction of diphenoxydiphenylsilicane seems to prove that at one stage sodium phenoxide is formed, and reacts with unchanged phenoxy-chloride to give the diphenoxy-derivative; this view is confirmed by the fact that sodium phenoxide is present in the blue insoluble residue (p. 2731). It does not seem likely, however, that symmetrical diphenoxytetraphenylsilicoethane is produced and then reacts with sodium to give sodium phenoxide, because, although some ethers are attacked by the metal (Schorigin, *Ber.*, 1926, **59**, 2510), diphenoxydiphenylsilicane and diethoxydiphenylsilicane (Kipping and Murray, this vol., p. 2736) appear to be unacted on. It may be suggested, therefore, that the phenoxy-chloride is decomposed by sodium, giving first $SiPh_2Cl{\cdot}SiPh_2Cl$ and then

$$SiPh_2Cl{\cdot}[SiPh_2]_2{\cdot}SiPh_2Cl,$$

and that a part of the latter is transformed into octaphenylsilicotetrane, whilst some of it reacts with sodium phenoxide to form diphenoxyoctaphenylsilicotetrane. The absence from the reaction product of (B), (C), and (D), however, does not accord with these assumptions, since it would seem to be highly probable that (B) at any rate would also be formed from such dichlorides.

Experimental.

Interaction of Phenol and Diphenylsilicon Dichloride.—Phenol (1 mol.), dissolved in a little benzene, is dropped slowly into diphenylsilicon dichloride * at about 150°, hydrogen chloride being immediately evolved; the liquid is then heated at about 200° until the evolution ceases (about 3 hours). The product deposits crystals of diphenoxydiphenylsilicon when it is kept at 0°, but it is more convenient to separate the latter by distillation (40 mm.). The first fraction (15—20%) is collected at about 200—240°, a large fraction (about 45%) at 250—260°, and a second large fraction at 280—310°, leaving a small residue. The liquid collected from 200—240°, when again treated with about one-half of its weight of phenol, gave further quantities of the two phenoxy-derivatives, but no fraction having the boiling point of diethoxydiphenylsilicane, a possible impurity in the diphenylsilicon dichloride, could be isolated.

Phenoxydiphenylsilicyl chloride, $SiPh_2Cl{\cdot}OPh$, obtained by the further fractionation of the liquid, b. p. about 250—260°, is a thick oil which barely fumes in the air and is miscible with light petroleum and other anhydrous solvents; it boils at 252—254°/40 mm. [Found: Cl, 11·0, 10·9, 11·2, 11·1 (four different preparations);

* Three samples of the dichloride (b. p. 224—226°/100 mm.) were used, containing 25·2, 24·8, and 25·7% of chlorine, respectively. (Calc. for $SiPh_2Cl_2$: Cl, 27·9%.) Compare Kipping and Murray, *loc. cit.*

Si, 9·0. $C_{18}H_{15}OClSi$ requires Cl, 11·4; Si, 9·1%]. It is immediately and completely soluble in a 5% solution of potassium hydroxide, giving the potassium derivatives of phenol and of diphenylsilicanediol. When left exposed to moist air, it is gradually converted into a solid, smelling strongly of phenol, which after recrystallisation from benzene consists of trianhydrotrisdiphenylsilicanediol.

Diphenoxydiphenylsilicane, $SiPh_2(OPh)_2$, separates in crystals from the fraction collected above 280°, but as it is always mixed with a considerable proportion of the oily phenoxy-chloride the crude product is fractionated again; it then crystallises from light petroleum in massive, colourless prisms and octahedra, m. p. 70—71° (Found: Si, 7·7, 7·8. $C_{24}H_{20}O_2Si$ requires Si, 7·7%). It is very readily soluble in ether, chloroform, benzene, or acetone, but only moderately soluble in cold alcohol. It can be recrystallised from the last-named solvent, but the crystals seem rather sticky and melt at 65—69°, doubtless owing to some very slight hydrolysis having occurred; if attempts are made to recrystallise the impure substance, containing phenoxy-chloride, from alcohol, complete decomposition results, and trianhydrotrisdiphenylsilicanediol may separate. When boiled with water for a short time, the diphenoxy-derivative is not appreciably hydrolysed, owing to its insolubility; it is also relatively stable towards a 5% solution of sodium hydroxide, but it is very readily hydrolysed in presence of acetone or alcohol with separation of trianhydrotrisdiphenylsilicanediol, whilst sodium phenoxide remains in solution. The fact that diphenoxydiphenylsilicane is present in a toluene solution which has been boiled during several hours with excess of sodium, is conclusive evidence of its stability under such conditions, and yet when an apparently pure specimen, recrystallised from light petroleum and melting sharply at 70—71°, is heated with sodium and a little toluene a distinct effervescence occurs and the metal is coated with a white powder. The reaction, however, soon ceases and the rest of the phenoxy-compound is unaltered. It would seem from these observations, repeated several times, that the recrystallised substance contains a small proportion of diphenylsilicanediol or phenoxyhydroxydiphenylsilicane.

Action of Sodium on Phenoxydiphenylsilicyl Chloride.—Freshly distilled phenoxy-chloride is dissolved in dry toluene (about 4 vols.), excess of sodium added, and the whole heated; an exothermic reaction soon sets in and the metal becomes coated with a blue crust similar to that obtained with diphenylsilicon dichloride under the same conditions. After the solution has boiled during 2—3 hours it contains some colourless crystals and seems to be free from phenoxy-chloride when tested with a copper wire. The hot solution

is filtered, the blue residue (I) washed with toluene, and the combined filtrate and washings are evaporated under reduced pressure. The almost colourless, oily product, when mixed with a little light petroleum (b. p. 50—60°), gives a crystalline precipitate (II), and the filtered solution, diluted with more petroleum, gives an oily separation (III); the clear petroleum solution, decanted from the oil, gives a further oily deposit (IV) when it is kept at 0°, but even then it contains a considerable quantity of product (V).

Isolation of octaphenylsilicotetrane. The blue residue (I) of sodium, sodium chloride, and sodium phenoxide is added in small portions to alcohol–acetic acid, the solution being kept acid; the insoluble matter, after being well washed with water, consists of almost pure octaphenylsilicotetrane, which was fully identified by a mixed melting-point determination, by its characteristic action with nitrobenzene and with iodine (compare Kipping and Sands, *loc. cit.*), and in other ways. So far as could be ascertained, the silicohydrocarbons (C) and (D) which are formed together with octaphenylsilicotetrane by the action of sodium on diphenylsilicon dichloride are not produced from the phenoxy-chloride; all the organic matter from the blue residue is soluble in boiling benzene, and although the final mother-liquors and the deposits were carefully examined, not a single crystal of (C) could be detected (compare Kipping, J., 1924, **125**, 2294).

Diphenoxyoctaphenylsilicotetrane, $PhO{\cdot}[SiPh_2]_4{\cdot}OPh$. The precipitate (II) consists of diphenoxyoctaphenylsilicotetrane and octaphenylsilicotetrane. The former is extracted with boiling benzene, in which it is much the more soluble, and is then recrystallised from boiling chloroform and again from benzene, from which it separates in well-defined, rhomboidal pyramids and in prisms, m. p. 215—216° (Found: Si, 12·3; C, 78·1; H, 5·2; *M*, in camphor, 1083, 1040. $C_{60}H_{50}O_2Si_4$ requires Si, 12·3; C, 78·7; H, 5·5%; *M*, 915). The diphenoxy-compound is decomposed when it is heated with piperidine and a concentrated solution of sodium hydroxide, giving the sodium derivatives of phenol and diphenylsilicanediol, with evolution of hydrogen. [Hydrogen value (compare Kipping and Sands, J., 1921, **119**, 848) found, 69·0, 67·4, 70·5; calc. for $PhO{\cdot}[SiPh_2]_4{\cdot}OPh + 10NaOH = 2PhONa + 4SiPh_2(ONa)_2 + 2H_2O + 3H_2$, 73·1].

Diphenoxyoctaphenylsilicotetrane is practically insoluble in ether, acetone, alcohol, and glacial acetic acid, and is far less soluble in cold benzene and chloroform than octaphenyl*cyclo*silicotetrane (B): it is so like the rhomboidal oxide (Kipping and Sands, J., 1921, **119**, 844) in crystalline form, solubilities, and melting point that it might well be mistaken for the latter, but its mixture with the rhomboidal

oxide melts at 208—211°. It is very readily soluble in boiling aniline, from which it separates on cooling in small prisms. It seems to be unchanged when it is heated during 1—2 hours with a glacial acetic acid solution of nitric acid, and it is so slowly hydrolysed when it is boiled with an alcoholic solution of hydrochloric acid that after about 20 hours' heating most of the substance remains undissolved and unchanged; the presence of phenol in the resulting pink solution can, however, be proved. The stability of the compound may be attributed to steric hindrance; its formation from the phenoxy-chloride under the above-described conditions is all the more noteworthy in view of the non-production of decaphenylsilicotetrane by the action of magnesium phenyl bromide on octaphenylsilicotetrane di-iodide (Kipping, J., 1923, **123**, 2602).

Other products from the phenoxy-chloride. From the combined oily separations (III) and (IV), by fractional extraction with light petroleum, diphenoxydiphenylsilicane was isolated and then, with the aid of a mixture of acetone and light petroleum, some diphenylsilicanediol, which had no doubt been formed by the hydrolysis of the diphenoxy-derivative during the prolonged fractionation with undried solvents. The mother-liquors from the diol gave on evaporation a glue-like mass, smelling strongly of phenol, which did not crystallise in the course of some weeks; after being washed with water and dissolved in acetone, this glue was precipitated by alcohol as a white curd, very similar in properties to the precipitates of (E_1) obtained in like manner (this vol., p. 2723). This product was redissolved and reprecipitated many times and then repeatedly extracted with warm alcohol, in which it was only very sparingly soluble; the warm glue was then drawn into threads and when cold the brittle mass was powdered and freed from solvent. Two different preparations gave Si, 13·3 and 13·6%, respectively; when hydrolysed with piperidine and sodium hydroxide, they gave hydrogen, sodium phenoxide, and the sodium derivative of diphenylsilicanediol, and the following hydrogen values: 82·7, 80·3, 81·1. These results agree with those required for

$$HO{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}OPh,$$

but the physical properties of the material do not seem to correspond with such a formula; possibly the substance is an oxide, $(PhO{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot})_2O$.

The light petroleum solution of the product (V) gave on evaporation a very thick, colourless oil, which in the course of some months deposited a considerable proportion of diphenoxydiphenylsilicane; this was removed by repeated extraction with warm alcohol. The residue was then completely and readily soluble in cold light petroleum (b. p. 40—50°), from which it separated as an oil. This product

contained 10·9% of silicon and is possibly impure symmetrical diphenoxytetraphenylsilicoethane, $PhO{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}OPh$, which requires Si, 10·3%; it gave hydrogen with acetone and sodium hydroxide, and the alkaline solution then contained sodium phenoxide and the sodium derivative of diphenylsilicanediol.

The author wishes to express his indebtedness to Mr. R. Vyle, M.Sc., who rendered very efficient assistance during this work, and to the Government Grant Committee of The Royal Society for funds from which to buy diphenylsilicon dichloride from Boots' Pure Drug Co.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 9th*, 1927.]

CCCLXIV.—*Organic Derivatives of Silicon. Part XXXV. The Preparation of Diphenylsilicon Dichloride: "Grignard" Ether and its Action on Silicon Tetrachloride.*

By FREDERIC STANLEY KIPPING and ARTHUR GEORGE MURRAY.

THE analysis of the first sample of diphenylsilicon dichloride gave 28·0% of chlorine (Calc. for $SiPh_2Cl_2$: Cl, 27·9%).* Large quantities of this compound were used later for the preparation of diphenylsilicanediol, and during a very careful examination of the latter and of its condensation products (J., 1912, **101**, 2108, 2125) there was no indication of unknown impurity in the dichloride. When, however, it was discovered that the product (E) contained phenoxy-compounds (this vol., p. 2720), several samples of the dichloride were examined and found to contain only 23—24% of chlorine; † they also gave 3—4% of phenol on hydrolysis.

The preparation of the magnesium phenyl bromide used in making the silicon compound was then carried out in an atmosphere of nitrogen (compare this vol., p. 2728), as was also, later on, the actual preparation of the dichloride; the samples thus obtained (b. p. 223—224° or 224—225°/100 mm.) gave inappreciable quantities of phenol, but still contained only 25·5—26% of chlorine, a proportion which could not be altered by further fractionation under various pressures. The silicon percentages in such samples agreed very closely with that required for $SiPh_2Cl_2$, an indication that the

* J., 1912, **101**, 2114. The sample was prepared and purified by one of us (F. S. K.), but was analysed under direction by a senior student, ignorant of the nature of the substance.

† The purchased samples were invoiced as having a purity of 80–90%.

impurity might be $SiPh_2(OEt)_2$ or $SiPh_2(OEt)Cl$, formed from traces of alcohol in the large volume of ether used in their preparation; but no matter how thoroughly the Grignard ether was freed from alcohol, the purity of the dichloride could not be increased and all samples gave alcohol on hydrolysis.

The behaviour of silicon tetrachloride towards ether was then studied (the tetraiodide is known to react; Friedel, *Ber.*, 1872, **5**, 27) and it was found that even at the ordinary temperature a slight action occurs, probably as follows: $SiCl_4 + Et_2O = SiCl_3 \cdot OEt + EtCl$. The difficulty of preparing pure diphenylsilicon dichloride is therefore almost certainly due to the formation of ethoxydiphenylsilicyl chloride, which cannot be separated by distillation (p. 2736).

As a solution of magnesium phenyl bromide could not be obtained without the use of ether, the method of preparation of the dichloride was modified so as to limit the interaction of the ether and the tetrachloride. The results were fairly satisfactory, but the product still contained a small proportion of some ethoxy-compound.

The fact that ether reacts with silicon tetrachloride probably accounts for previous difficulties in preparing various organic derivatives of silicon. Thus from the product of the interaction of magnesium ethyl bromide and the tetrachloride, it may not be hard to obtain ethylsilicon trichloride, but the isolation of the di- and the tri-ethyl derivatives by fractional distillation is a very troublesome task (J., 1909, **95**, 311); the difficulty of preparing a pure sample of phenylethylsilicon dichloride (J., 1907, **91**, 217) is also possibly due to the contamination of the product with ethoxyphenylethylsilicyl chloride. In the case of a crystalline product, the formation of some ethoxy-compound would not matter so much, as the impurity would doubtless remain in the mother-liquor; this has been proved to be so in the case of dibenzylsilicon dichloride, since the liquid fractions from the crude preparation give ethyl alcohol on hydrolysis.

Experimental.

For the detection of phenoxy- and ethoxy-groups in an ordinary sample of diphenylsilicon dichloride, the latter is dropped into excess of a 5% solution of sodium hydroxide, and a small proportion of the liquid is then distilled and tested for alcohol; the residue is acidified and again distilled and the distillate is treated with bromine water. Samples of the dichloride prepared by the method described later do not give a recognisable quantity of tribromophenol.

Interaction of Ether and Silicon Tetrachloride.—Very carefully

purified ether was heated under reflux during about 4 hours with an equal volume of silicon tetrachloride; about one-half of the liquid was then distilled and the residue was treated with an excess of sodium hydroxide solution and again distilled; the first small portion of the aqueous distillate gave a distinct but very slight iodoform reaction. By heating the recovered ether (20 c.c.) with about 5% of silicon tetrachloride in a sealed tube during about 8 hours at 100° and then proceeding as before, about four times as much iodoform was obtained, but even under these conditions the quantity was only about 5 mg. The interaction also occurs at the ordinary temperature; after 30 c.c. of ether had been left with about 5 c.c. of silicon tetrachloride during 3 days and most of the ether then distilled off, the residue, on hydrolysis, gave enough alcohol to afford a very slight precipitate of iodoform, and the ether which had been distilled from the mixture, treated again with the tetrachloride, gave a further quantity of the product which yielded alcohol; these processes were repeated four times, with the ether recovered from each previous treatment, and iodoform was obtained, apparently in much the same quantity, after each set of operations.* As the precipitate of iodoform was not appreciably larger than usual when the mixture had been kept during several weeks, it would seem that the reaction is reversible.

Diethoxydiphenylsilicane, $SiPh_2(OEt)_2$, was prepared in order to compare its boiling point with that of diphenylsilicon dichloride. Carefully dehydrated alcohol, in slight excess, was added to the dichloride; only a feeble evolution of hydrogen chloride occurred and two layers were formed, but after having been heated under reflux during 6—8 hours the liquid became homogeneous and was then distilled (100 mm.). The product still contained a little chlorine, and was therefore heated again with a small proportion of alcohol and then fractionated; practically the whole passed over at 217—218°, and a considerable quantity of the preparation gave only an insignificant reaction with an aqueous solution of silver nitrate [Found: Si, 10·4. $SiPh_2(OEt)_2$ requires Si, 10·4%]. The b. p. of the diethoxy-compound differs only very little from that of the dichloride,

$SiPh_2(OEt)_2$	197—198°/50 mm.	217—218°/100 mm.	302—304°/767 mm.
$SiPh_2Cl_2$	199—202°/50 mm.	222—224°/100 mm.	302—305°/757 mm.

* A blank experiment in which ether alone was heated under reflux with a solution of sodium hydroxide during 4 hours, and the alkaline solution was then tested for alcohol, gave a negative result and did not confirm the statement in Allen's "Commercial Organic Analysis" (vol. I, p. 179) that ether kept in presence of moisture generates traces of alcohol.

and it may therefore be deduced that that of the ethoxy-chloride, $SiPh_2Cl{\cdot}OEt$, would differ even less, so that its separation from the dichloride by distillation would be impossible.

Diethoxydiphenylsilicane is specifically heavier than water and is miscible with the common solvents; it seems to be unchanged when it is left during some hours with a 5% solution of potassium hydroxide, but it is quickly hydrolysed by an alcoholic solution and when only a little alkali is present trianhydrotrisdiphenylsilicanediol may separate in crystals; it is also slowly hydrolysed by dilute sulphuric acid. It appears to be unchanged by sodium at 100°.

Preparation of Diphenylsilicon Dichloride.—Silicon tetrachloride (170 g.), diluted with benzene (3 vols.), is placed in a bulb provided with three tubulures, which is fitted with a stirrer and a reflux condenser and is connected through a dropping-funnel with the apparatus for the preparation of magnesium phenyl bromide ($2\frac{1}{4}$ mols.). The air in the whole apparatus is displaced with dry nitrogen and the Grignard reagent is then prepared at 0°, the minimum quantity of ether being used. When about one-half of the magnesium has been dissolved, the ethereal solution is drawn into the exhausted dropping-funnel and is then slowly added to the well-cooled and stirred tetrachloride while the remainder of the Grignard reagent is being made. This portion is then drawn into the funnel as before and added to the tetrachloride, so that at no stage is there any possibility of oxidation. After the product has been stirred during a further period of about 30 minutes, as much ether as possible is distilled off on a water-bath, the operation lasting about 3 hours. More benzene (2 vols.) is then added and the magnesium salts are separated in the usual apparatus (J., 1907, **91**, 216) and well washed with benzene. The combined filtrate and washings give on evaporation such a small deposit of magnesium salt that a second filtration is unnecessary (J., 1912, **101**, 2114) and the product can be directly fractionated. Samples thus obtained contain 27·2—27·3% of chlorine.

The authors wish to express their thanks to the Government Grant Committee of the Royal Society for funds which enabled them to purchase supplies of diphenylsilicon dichloride from Boots' Pure Drug Co., Ltd.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 9th*, 1927.]

CCCLXV.—*The Condensation of* o-*Aminothiophenol with* αβ-*Unsaturated Acids.*

By William Hobson Mills and James Bell Whitworth.

In the course of some experiments carried out with *o*-aminothiophenol with the view of synthesising a carbothiocyanine dye (J., 1922, **121**, 455), we found that this base reacted in an unexpected manner with glutaconic acid. The two substances interacted very readily when heated together, but the product of the reaction was not the anticipated benzthiazole derivative; it was a new compound formed by the condensation of one molecule of glutaconic acid and one molecule of aminothiophenol, with the elimination of one molecule of water, as shown in the equation

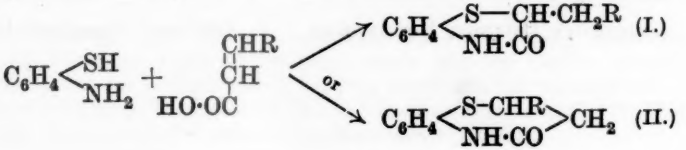
$$C_6H_7NS + C_5H_6O_4 = C_{11}H_{11}O_3NS + H_2O.$$

It was a monobasic acid and it showed none of the reactions characteristic either of the ethylenic linking, the thiol group, or the amino-group. In the interaction, therefore, both the thiol group and the amino-group of the aminothiophenol and the ethylenic linking and one of the carboxyl groups of the glutaconic acid are concerned. That addition of some group to the ethylenic linking had occurred was further indicated by the fact that the new compound was resolvable into antimeric optically active forms, for it would seem that the only way in which an asymmetric carbon atom could be produced in its molecule would be through addition to this linking.

The behaviour of the following αβ-unsaturated acids towards *o*-aminothiophenol was then examined: acrylic, crotonic, and cinnamic acids, and they were all found to react with it similarly to glutaconic acid.

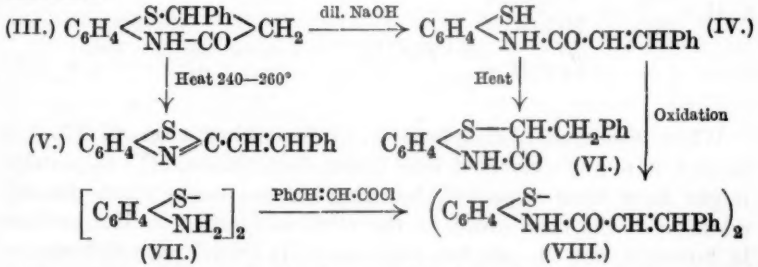
There are four ways in which the observed condensations might occur:

In the first place, *addition of the thiol group* of the aminothiophenol to the ethylenic linking of the acid might take place, accompanied by condensation between the amino- and carboxyl groups. This would give two possible formulæ, according as the sulphur was attached (1) to the α-carbon atom (formation of a ketodihydro-1 : 4-benzthiazine derivative, I), or (2) to the β-carbon atom (formation of a ketotetrahydro-1 : 5-heptabenzthiazine derivative, II).



Alternatively, *addition of the amino-group* of the aminothiophenol to the ethylenic linking of the acid might occur, with condensation between the carboxyl and thiol groups. This would give two further possible constitutions—(3) and (4)—according to whether the nitrogen was attached to the α- or the β-carbon atom.

We found that actually condensation of the amino-group of the aminothiophenol with the carboxyl group of the acid had occurred and that therefore addition of the thiol group to the ethylenic linking had taken place. This was established by examining the compound obtained from cinnamic acid and aminothiophenol. The resulting compound was an indifferent substance, but on being heated with dilute alkalis it dissolved gradually, forming a yellow solution from which carbon dioxide precipitated an isomeric compound, which could be proved to have the constitution (IV); for it had all the properties of a thiophenol, being soluble in alkalis, giving a mercuric derivative with mercuric chloride, and being converted by atmospheric oxygen and various other oxidising agents—iodine, ferric chloride, or hydrogen peroxide—with loss of one atom of hydrogen into a compound insoluble in alkalis, which was shown to be the disulphide (VIII), since it could be synthesised by introducing a cinnamoyl group into each of the two amino-groups of *oo'*-diaminodiphenyl disulphide (VII), by treatment with cinnamoyl chloride.

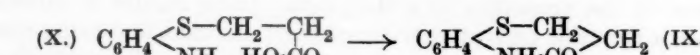


These observations limit the possible formulæ for the compound to (I), the ketodihydrobenzthiazine, or (II), the ketotetrahydroheptabenzthiazine (R = Ph). The behaviour towards alkalis, however, is different from that recorded for the ketodihydrobenzthiazines, which, according to Unger and Graff (*Ber.*, 1897, **30**, 2387), undergo, on boiling with potash, fission of the heterocyclic ring between the -NH- and -CO- groups. Further, the compound could be shown definitely not to be a ketodihydrobenzthiazine, since it was different from the *keto-2-benzyldihydrobenzthiazine* (VI) we obtained, according to the general method described by Unger and Graff (*loc. cit.*) for preparing these compounds, by heating *o*-aminothiophenol with α-bromo-β-phenylpropionic acid.

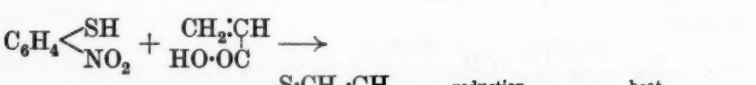
Similarly, our products from acrylic acid and crotonic acid and aminothiophenol are different from the keto-2-methyldihydrobenzthiazine and the keto-2-ethyldihydrobenzthiazine obtained by Unger and Graff from α-bromopropionic acid and α-bromobutyric acid and aminothiophenol; also we found that α-bromoglutaric acid (employed in the form of its ester) gave a different product from that obtained with glutaconic acid.

The compounds in question are therefore ketotetrahydroheptabenzthiazines of the general formula (II).

A final confirmation of the correctness of this conclusion was secured by showing that the compound got by heating aminothiophenol with acrylic acid is identical with the ε-lactam (IX) obtained by Mayer and Horst (*Ber.*, 1923, **56**, 1415) by heating β-2-aminophenylthiolpropionic acid (X), and further by the synthesis of this

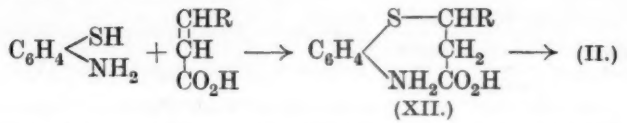


compound from *o*-nitrothiophenol and acrylic acid, as follows, the initial condensation evidently consisting in β-addition of the thiol group of the nitrothiophenol to the ethylenic linkage of the acrylic acid:



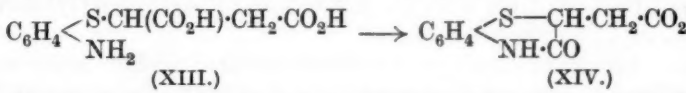
When *cinnamamidothiophenol* (IV) (see scheme on p. 2739) is heated, it is not converted into 1-styrylbenzthiazole (V) as perhaps might have been expected, but ring closure takes place through addition of the thiol group to the ethylenic linkage. The product is, however, not the original ε-lactam (III) (*keto-2-phenyltetrahydroheptabenzthiazine*), but the isomeric δ-lactam (VI) (keto-2-benzyldihydrobenzthiazine), the sulphur becoming attached to the α-carbon atom of the ethylenic linking. The tendency to the formation of a six- rather than of a seven-membered ring thus over-rides the natural tendency of the sulphur atom of the thiol group to attach itself to the β-carbon atom of the ethylenic linking (Posner, *Ber.*, 1907, **40**, 4788). It follows from this fact that, in the interaction of the αβ-unsaturated acids with *o*-aminothiophenol, of the various reactions possible that which takes place with the greatest velocity (excluding of course salt formation between the acid and base) is the addition of the thiol group to the ethylenic linking, the sulphur becoming attached to the β-carbon atom, the resulting aminophenyl-

thiolpropionic acid (XII) passing, at the temperature employed, with loss of water into its ε-lactam :



(XII.)

To test this conclusion, the interactions of *o*-aminothiophenol with maleic acid and with monobromosuccinic acid were studied. In all the other cases investigated, we have seen that a different product was obtained according as *o*-aminothiophenol was heated with a given αβ-unsaturated acid or with the corresponding α-bromosaturated acid. In this one case, however, identical products should be formed, since in the intermediate product (XIII) arising from maleic acid there is, besides the carboxyl group to which, as in the other cases, the amino-group is in the ε-position, a second carboxyl group to which it is in the δ-position and with which it can consequently react, producing a normal six-membered ring :



(XIII.) (XIV.)

The result was as expected, the same product (*3-ketodihydrobenzthiazine-2-acetic acid*, XIV) being obtained by heating either maleic acid or monobromosuccinic acid with *o*-aminothiophenol.

If the ε-lactam (keto-2-phenyltetrahydroheptabenzthiazine, III obtained by heating *o*-aminothiophenol with cinnamic acid is heated to 240—260°, water is eliminated and there is formed, although not very smoothly, 1-styrylbenzthiazole (V). This explains why Hofmann (*Ber.*, 1880, **13**, 1235) had obtained from *o*-aminothiophenol and cinnamic acid this benzthiazole derivative, whilst we had found the product of the reaction to be the ε-lactam; we had worked at 160—170°, whereas Hofmann had heated the mixture on a sand-bath. Hofmann's procedure does not, however, provide an advantageous method for preparing the benzthiazole base : it can be much more readily prepared by treating *o*-aminothiophenol (or, better, its sodium salt) with cinnamoyl chloride in the cold. On the other hand, we found that the corresponding saturated acid, β-phenylpropionic acid, reacted readily with *o*-aminothiophenol to give phenylethylbenzthiazole.

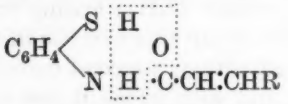
If *o*-aminothiophenol is heated with ethyl cinnamate instead of with cinnamic acid, a higher temperature has to be employed to bring about reaction, and the product is then the δ-lactam (keto-2-benzyldihydrobenzthiazine, VI).

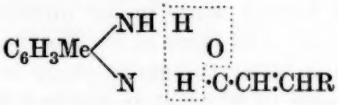
Thus, according as *o*-aminothiophenol is heated with cinnamic

acid, its ester, or its chloride, three different heterocyclic compounds are obtained.

o-Aminothiophenol
- —(cinnamic acid)→ Ketophenyltetrahydroheptabenzthiazine (III).
- —(ethyl cinnamate)→ Ketobenzyldihydrobenzthiazine (VI).
- —(cinnamoyl chloride)→ Styrylbenzthiazole (V).

The non-formation of a benzthiazole base when *o*-cinnamamidothiophenol (IV) is heated, or when ethyl cinnamate is heated with *o*-aminothiophenol, shows that the attachment of a $-CH{:}CHR$ group, instead of a saturated system, to the carbon of the $-CO{\cdot}NH-$ group in *N*-acyl derivatives of *o*-aminothiophenol makes the elimination of water in the manner shown more difficult.





The corresponding phenomenon was observed by Fichter (*J. pr. Chem.*, 1906, **74**, 316) with the crotonyl and dimethylacrylyl derivatives of 1 : 3 : 4-tolylenediamine.

The ketotetrahydroheptabenzthiazines are readily acetylated when boiled with acetic anhydride. This was also observed by Mayer and Horst, who found (*loc. cit.*) that their ε-lactam reacted easily with acetic anhydride. However, they assigned to the product the formula (XV), which is at variance with the composition we find for it and for the two corresponding derivatives which we have obtained from our analogous ε-lactams; the molecule is actually less by the elements of a molecule of water than this formula indicates. It is also at variance with the chemical character of the compounds: they are neutral and unaffected by cold

(XV.) $C_6H_4\langle^{S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}_{NHAc}$ $\quad$ $C_6H_4\langle^{S\text{--}CHR}_{NAc{\cdot}CO}\rangle CH_2$ (XVI.)

$C_6H_4\langle^{S{\cdot}CH_3}_{NH{\cdot}CO}\rangle CH_3$ (XVII.)

sodium carbonate solution. Since, moreover, the acetyl group is readily eliminated on warming with dilute hydrochloric acid or sodium carbonate with regeneration of the original lactam, the constitution of these acetyl derivatives is clearly that represented by (XVI). Their ready formation is in accordance with the fact observed by Ulffers and von Janson (*Ber.*, 1894, **27**, 93) and by Sudborough (J., 1901, **79**, 533) that diacetylation of a primary aromatic amine is particularly easy when there is another substituent group in the ortho-position to the amino-group. These ε-lactams are closely related in constitution to *o*-acetamidothio-

anisole (XVII) (linking of the two methyl groups in which, with removal of two atoms of hydrogen, would yield the ε-lactam of Mayer and Horst), and Mr. G. E. Watts, working in this laboratory, found that *o*-aminothioanisole is readily converted into a diacetyl derivative when heated with acetic anhydride.

An interesting alternation in properties exists between the γ-, δ-, and ε-lactams, benzthiazolone (XVIII), ketodihydrobenzthiazine (XIX), and ketotetrahydroheptabenzthiazine (IX), with respect to

(XVIII.) $C_6H_4\langle{}^{S-}_{NH}\rangle CO$ $\qquad$ $C_6H_4\langle{}^{S—CH_2}_{NH\cdot CO}$ (XIX.)

acetylation. Benzthiazolone (for which a new method of preparation is described in the experimental part) and, as has been stated, the ε-lactam (IX) are readily acetylated when boiled with acetic anhydride, whilst ketodihydrobenzthiazine is not (Unger and Graff, *loc. cit.*).

Experimental.

I. *Glutaconic Acid and* o-*Aminothiophenol.*

4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetic Acid* (II; R = $CH_2\cdot CO_2H$).—A mixture of glutaconic acid (2·5 g.) and *o*-aminothiophenol (2·5 g.; 1 mol.) was heated in an atmosphere of carbon dioxide at 120—130° for 20 minutes. A vigorous reaction occurred and after a few minutes the whole had set to a crystalline mass, which, recrystallised from dilute alcohol or water, yielded the pure product as thin, colourless, silky needles, m. p. 235—236° (decomp.). Yield, 4 g. (84·4%) (Found : C, 55·5; H, 4·6. $C_{11}H_{11}O_3NS$ requires C, 55·7; H, 4·6%).

The compound dissolves readily in dilute aqueous sodium carbonate and can be sharply titrated against sodium hydroxide and phenolphthalein [0·2607 g. required 11·1 c.c. *N*/10-NaOH. Found : *M*, 234·8 (monobasic). $C_{11}H_{11}O_3NS$ requires *M*, 237]. It has no marked basic properties, dissolving in hot, concentrated hydrochloric acid and crystallising unchanged on cooling. It is soluble in acetone or glacial acetic acid, sparingly soluble in ether, and practically insoluble in benzene, ligroin, or chloroform.

The *ethyl* ester was prepared by keeping the acid (1 g.) in excess of cold, absolute alcohol, containing dry hydrogen chloride, for 24 hours; when the resulting solution was diluted, and neutralised with sodium carbonate, the *ester* separated in small, lustrous, colourless needles (0·8 g.), which, after recrystallisation from benzene–ligroin, melted at 139—140° (Found : C, 58·7; H, 5·7. $C_{13}H_{15}O_3NS$ requires C, 58·9; H, 5·7%). It is readily soluble in alcohol, ether, or benzene, and sparingly soluble in ligroin.

The ester was also obtained directly from ethyl glutaconate: A mixture of ethyl glutaconate (1 mol.) and *o*-aminothiophenol (1 mol.) was heated under reflux, in an atmosphere of carbon dioxide, at 160—180° for 3 hours; a brown gum was then obtained, from which some crystals separated on standing. The crystalline product was extracted from the gum with hot ligroin, from which it separated on cooling in small, colourless, glistening needles, m. p. 138—140°. A mixture with the ester prepared as described above melted at 139—140°.

Resolution of 4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetic Acid into Optically Active Components.*—d-4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetic acid.* From a solution of the *dl*-acid (4·7 g.) and anhydrous brucine (7·9 g.) in warm alcohol (60 c.c.) the brucine salt was rapidly deposited in small, soft, colourless needles. After cooling, the salt was collected and recrystallised three times from alcohol; its specific rotation then became constant. The l-*brucine* d-4-*ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetate* so obtained gave m. p. 164—165° (softening at 155°) and $[\alpha]^{20°}_{5461}$ +154·7° in aqueous solution ($l = 2$; $c = 0{\cdot}527$). On decomposition of this salt with cold, dilute hydrochloric acid, the d-*acid* was deposited in fine, colourless needles, which on recrystallisation from alcohol gave the pure *d*-acid (1 g.), m. p. 230° and $[\alpha]^{20°}_{5780}$ +436·9°, $[\alpha]^{20°}_{5461}$ +506°, $[\alpha]^{20°}_{4359}$ +981° in absolute ethyl alcohol ($l = 2$; $c = 0{\cdot}6008$) (Found: C, 56·0; H, 4·7. $C_{11}H_{11}O_3NS$ requires C, 55·7; H, 4·6%).

Ethyl d-4-*ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetate* was obtained by treating the pure *d*-acid with cold alcoholic hydrogen chloride. It separated from benzene–ligroin in short, thin, colourless needles, m. p. 145—146° and $[\alpha]^{20°}_{5780}$ +424·5°, $[\alpha]^{20°}_{5461}$ +491·7°, $[\alpha]^{20°}_{4359}$ +948·8° in absolute alcohol ($l = 2$; $c = 0{\cdot}5512$).

1-4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetic acid.* The crude *l*-acid (1·7 g.), recovered from the mother-liquor of the above described brucine salt, and cinchonine (2·2 g.), were dissolved in alcohol (12 c.c.). After the addition of ether, the cinchonine salt gradually separated in small, colourless prisms, which were recrystallised twice from aqueous alcohol; m. p. 193—195° (softening at 175—180°). This salt, decomposed with cold, dilute hydrochloric acid, gave the pure l-*acid* (0·5 g.) in microscopic, colourless needles, m. p. 229—230° and $[\alpha]^{20°}_{5780}$ −435·5°, $[\alpha]^{20°}_{5461}$ −505°, $[\alpha]^{20°}_{4359}$ −976° in absolute ethyl alcohol ($l = 2$; $c = 0{\cdot}6004$).

Ethyl 3-*Keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*propionate* (I; R = $CH_2{\cdot}CO_2Et$).—This compound was synthesised for comparison with the compound obtained from *o*-aminothiophenol and glutaconic acid. It melts at 91°, whilst the isomeric ethyl ketotetrahydro-1 : 5-heptabenzthiazine-2-acetate melts at 139—140°.

o-Aminothiophenol (3·4 g.; 2 mols.) and ethyl α-bromoglutarate (3·2 g.) were heated together under reflux, in an atmosphere of carbon dioxide, at 120—130° for an hour; a brisk reaction then occurred with elimination of alcohol and formation of a crystalline material (hydrobromide). The crude product was extracted with hot ligroin, from which *ethyl 3-keto-2 : 3-dihydro-1 : 4-benzthiazine-2-propionate* separated in small, colourless, silky needles; these, after recrystallisation from ligroin, melted at 91° (Found: C, 58·8; H, 5·6. $C_{13}H_{15}O_3NS$ requires C, 58·9; H, 5·7%). The residue remaining after the extraction of the ester consisted of the hydrobromide of *oo'*-diaminodiphenyl disulphide. On hydrolysis of the ester, 3-keto-2 : 3-dihydro-1 : 4-benzthiazine-2-propionic acid was obtained in colourless needles, m. p. 174—175°.

II. *Cinnamic Acid and* o-*Aminothiophenol.*

4-Keto-2-phenyltetrahydro-1 : 5-heptabenzthiazine (III).—A mixture of *o*-aminothiophenol (8 g.) and cinnamic acid (10 g.) was heated for 2 hours under reflux, in an atmosphere of carbon dioxide, at 160—170°; a vigorous reaction then set in with elimination of water. On cooling, the product set to a hard, reddish-brown mass which, on crystallisation from alcohol, yielded *4-keto-2-phenyltetrahydro-1 : 5-heptabenzthiazine* in short, colourless, silky needles, m. p. 177°. Yield 11 g. (Found: C, 70·5; H, 5·0. $C_{15}H_{13}ONS$ requires C, 70·6; H, 5·1%).

The compound is soluble in chloroform, acetone, or glacial acetic acid, sparingly soluble in ether or benzene, and insoluble in water. It dissolves in hot concentrated hydrochloric acid and separates from the solution unchanged on cooling.

The *acetyl* derivative (XVI; R = Ph) was obtained by boiling the substance with excess of acetic anhydride for 15 minutes. It crystallised from alcohol in short, glistening, colourless needles, m. p. 155—156° (Found: C, 68·2; H, 5·0. $C_{17}H_{15}O_2NS$ requires C, 68·7; H, 5·0%). It is readily hydrolysed by warming on the water-bath with dilute hydrochloric acid, giving the original material.

The Sulphoxide, $C_6H_4<\begin{matrix}SO\cdot CHPh\\NH—CO\end{matrix}>CH_2$.—To a solution of the heptabenzthiazine (0·6 g.) in warm acetone (15 c.c.), a 4% solution of potassium permanganate in aqueous acetone was added until in slight excess, together with a little dilute sulphuric acid. The mixture was then boiled and filtered hot and the residue was extracted with hot acetone. The almost pure *sulphoxide* separated from the filtrate and was collected after dilution with water and cooling. It separated from acetone–alcohol or from dilute acetic

acid in clusters of thin, silky needles, m. p. 210° (Found: C, 66·4; H, 4·8. $C_{15}H_{13}O_2NS$ requires C, 66·4; H, 4·8%).

The sulphoxide is soluble in glacial acetic acid, sparingly soluble in alcohol or ether, and insoluble in water. It can also be obtained, in an almost pure condition, by treating the heptabenzthiazine with hydrogen peroxide (30%) in cold glacial acetic acid solution and diluting the mixture with water after several hours.

The Sulphone.—To a solution of the heptabenzthiazine (0·7 g.) in glacial acetic acid (10 c.c.), excess of 5% aqueous potassium permanganate (20 c.c.) was slowly added at room temperature, with stirring. The *sulphone* soon began to separate from the solution and after an hour the product was collected and recrystallised from dilute acetic acid, the solution being decolorised by charcoal. It was thus obtained in short, colourless, glistening needles, m. p. 234—235° (Found: C, 62·6; H, 4·6. $C_{15}H_{13}O_3NS$ requires C, 62·7; H, 4·5%).

The sulphone is moderately easily soluble in glacial acetic acid, sparingly soluble in alcohol or benzene, and insoluble in light petroleum, chloroform, or water. It is also formed when the heptabenzthiazine is oxidised by chromic acid in boiling glacial acetic acid solution.

Action of Alkali on 4-Keto-2-phenyltetrahydro-1 : 5-heptabenzthiazine: Formation of o-Cinnamamidothiophenol (IV).—When the heptabenzthiazine is heated for some time with excess of dilute caustic alkali solution, complete hydrolysis takes place into cinnamic acid and *o*-aminothiophenol. When, however, it is carefully heated with a small excess of caustic alkali, the product is *o-cinnamamidothiophenol.*

4-Keto-2-phenyltetrahydro-1 : 5-heptabenzthiazine (4 g.) was heated with 10% caustic potash solution (40 c.c.) and a little alcohol (8 c.c.) under reflux for 20—30 minutes, a deep yellow solution being obtained. After cooling, this was diluted with water and treated with carbon dioxide; *o*-cinnamamidothiophenol was then precipitated as a faintly yellowish-white, pasty mass. It crystallised from alcohol in clusters of small, almost colourless needles, m. p. 147—148°. Yield, 2 g. (Found: C, 70·6; H, 5·2. $C_{15}H_{13}ONS$ requires C, 70·6; H, 5·1%).

o-Cinnamamidothiophenol is readily soluble in acetone, chloroform, or benzene, and moderately easily soluble in ether or ligroin. It dissolves in caustic soda and slowly in sodium carbonate, giving yellow solutions, from which it is precipitated on acidification. It is readily oxidised to the corresponding disulphide by means of iodine, hydrogen peroxide or ferric chloride, or by exposure to the air.

The *mercurichloride* is precipitated when an alcoholic solution of the cinnamamidothiophenol is treated with aqueous mercuric chloride. It crystallises from alcohol, in which it is only sparingly soluble, in fine, colourless needles, m. p. 211—212°.

Conversion of o-*Cinnamamidothiophenol into* 3-*Keto*-2-*benzyl*-2 : 3-*dihydro*-1 : 4-*benzthiazine* (VI).—*o*-Cinnamamidothiophenol was heated in an atmosphere of dry carbon dioxide at 165—170° for 4—6 hours. The resulting dark, viscous liquid set, on cooling, to a hard, glassy mass, which was powdered and extracted with ether. The colourless, crystalline residue separated from alcohol in clusters of small, yellowish-white, silky needles. It proved to be 3-keto-2-benzyldihydro-1 : 4-benzthiazine and melted, alone or mixed with a specimen synthesised from α-bromo-β-phenylpropionic acid and *o*-aminothiophenol (see below), at 159—160°.

oo′-*Dicinnamamidodiphenyl Disulphide* (VIII).—(a) *From* o-*cinnamamidothiophenol.* From a solution of *o*-cinnamamidothiophenol (1 g.) in cold acetone (30 c.c.) to which excess of 30% hydrogen peroxide (2—3 c.c.) had been added, the *disulphide* soon separated as a mass of colourless, silky needles, which, after recrystallisation from acetone or glacial acetic acid, and when mixed with the pure disulphide synthesised as described below, melted at 163—164° (Found: C, 70·9; H, 4·8. $C_{30}H_{24}O_2N_2S_2$ requires C, 70·9; H, 4·7%).

(b) *From* oo′-*diaminodiphenyl disulphide* (VII). A solution of cinnamoyl chloride (2·6 g.) in dry benzene was gradually added to a solution of *oo′*-diaminodiphenyl disulphide (3·9 g.) in the same solvent. After 30 minutes, the pasty product was collected and treated with warm alcohol to remove the hydrochloride of the diaminodiphenyl disulphide, and the residue was crystallised from glacial acetic acid; pure *oo′*-dicinnamamidodiphenyl disulphide then separated in colourless, silky needles, m. p. 163—164° (Found: C, 71·0; H, 4·8%).

The disulphide is readily soluble in chloroform or hot benzene, sparingly soluble in alcohol, and insoluble in light petroleum.

Bromo-derivative. To a solution of *oo′*-dicinnamamidodiphenyl disulphide (0·5 g.) in dry chloroform (12 c.c.), a 10% solution of bromine in dry chloroform (6 c.c.) was gradually added; a colourless, pasty solid was then precipitated. After being washed with chloroform, this crystallised from acetone in small, glistening, colourless plates (0·4 g.), which darkened at 205° and melted at 213° (decomp.) (Found: C, 54·2; H, 3·6; Br, 23·8.

$$C_{30}H_{24}O_2N_2Br_2S_2$$

requires C, 53·9; H, 3·6; Br, 24·0%).

3-*Keto*-2-*benzyl*-2 : 3-*dihydro*-1 : 4-*benzthiazine* (VI).—(a) *From* α-*bromo*-β-*phenylpropionic acid.* A mixture of α-bromo-β-phenyl-

propionic acid (2·5 g.) and *o*-aminothiophenol (2 g.) was heated in an atmosphere of carbon dioxide at 125—130°; a vigorous reaction then set in and was complete after about 20 minutes. The crude product was crystallised twice from alcohol, pure 3-*keto*-2-*benzyl*-2 : 3-*dihydro*-1 : 4-*benzthiazine* being obtained in short, colourless, silky needles, m. p. 159—160° (1·6 g.) (Found: C, 70·3; H, 5·1. $C_{13}H_{15}ONS$ requires C, 70·6; H, 5·1%). This substance is readily soluble in acetone, chloroform, benzene, or glacial acetic acid and moderately easily soluble in ligroin or ether. It is insoluble in concentrated hydrochloric acid and in dilute caustic soda solution, but it dissolves in cold, concentrated sulphuric acid to a yellow solution, from which it is precipitated unchanged by water. It does not form an acetyl derivative.

(b) *From ethyl cinnamate.* A mixture of ethyl cinnamate (3 g.) and *o*-aminothiophenol (2 g.) was heated under reflux in an atmosphere of carbon dioxide at 230—240° for 4—5 hours. The crude product was a deep red, oily liquid, which, on treatment with ether, yielded a pale yellow, crystalline solid. Recrystallised from alcohol, this separated in small, faintly yellow, silky needles, m. p. and "mixed m. p." with pure 3-keto-2-benzyldihydro-1 : 4-benzthiazine synthesised as above, 159—160° (Found: C, 70·5; H, 5·0%).

1-*Styrylbenzthiazole* (V).—(a) *From cinnamoyl chloride.* The condensation of cinnamoyl chloride with *o*-aminothiophenol takes place readily in cold benzene solution, but the following method, using the sodium salt of the aminothiophenol, is more satisfactory.

To a solution of *o*-aminothiophenol (1·3 g.) and sodium (0·23 g.) in absolute alcohol (12 c.c.), cinnamoyl chloride (1·6 g.) was gradually added, the mixture warmed on the water-bath for a few minutes, and the solution filtered from the precipitated sodium chloride and concentrated. On cooling, 1-*styrylbenzthiazole* was deposited from the solution and on recrystallisation from alcohol it separated in short, thick, colourless prisms (1 g.), m. p. 112—113° (Found: C, 75·7; H, 4·8. $C_{15}H_{11}NS$ requires C, 75·9; H, 4·6%).

The *picrate* crystallised from alcohol, in which it is only sparingly soluble, in bright yellow platelets, m. p. 195—196°.

(b) *From* 4-*keto*-2-*phenyltetrahydro*-1 : 5-*heptabenzthiazine.* The thiazine was heated at 240—260° for about an hour; water was evolved and the fused mass changed to a dark brown gum, which set to a hard solid. This was crystallised twice from alcohol (charcoal) and 1-styrylbenzthiazole was then obtained in short, colourless prisms. These, alone or mixed with the pure base obtained by method (a), melted at 112—113°. The yield was poor.

(c) *From cinnamic acid* (compare Hofmann, *Ber.*, 1880, **13**, 1235).

Cinnamic acid (2 g.) and *o*-aminothiophenol (1·8 g.) were heated together at 210—220° for about 2 hours; a dark-coloured gum was obtained which was difficult to purify. On treatment with picric acid in alcoholic solution, however, the picrate of the benzthiazole base was precipitated, and after crystallisation from alcohol (charcoal), this was obtained in bright yellow platelets (1 g.), m. p. 195—196° (Found: C, 54·3; H, 2·9. $C_{21}H_{14}O_7N_4S$ requires C, 54·1; H, 3·0%).

The base was also obtained in small yield by heating together cinnamic acid and aminothiophenol at a higher temperature and treating the crude product with alkali, according to Hofmann's method. Its formation did not readily take place below about 220°.

β-*Phenylpropionic Acid and* o-*Aminothiophenol*: 1-β-*Phenylethylbenzthiazole*.—A mixture of β-phenylpropionic acid (1 mol.) and *o*-aminothiophenol (1 mol.) was heated under reflux in an atmosphere of carbon dioxide at 160—170° for 2 hours. The crude product was heated for a short time on the water-bath with 10% caustic soda solution; the yellow oil obtained solidified on cooling, and on crystallisation from dilute alcohol it yielded 1-β-*phenylethylbenzthiazole* in lustrous, colourless platelets, m. p. 60—61° (Found: C, 75·4; H, 5·5. $C_{15}H_{13}NS$ requires C, 75·3; H, 5·4%). The base is moderately easily soluble in cold alcohol and readily soluble in ether.

The *picrate* separates from alcohol in small, bright yellow plates, m. p. 132—133°.

III. *Crotonic Acid and* o-*Aminothiophenol.*

4-*Keto*-2-*methyltetrahydro*-1 : 5-*heptabenzthiazine* (II; R = Me).—A mixture of crotonic acid (1·3 g.) and *o*-aminothiophenol (1·8 g.) was heated in an atmosphere of carbon dioxide at 165—170° for 20 minutes. A vigorous reaction then occurred and the whole set to a crystalline mass, which, recrystallised from alcohol, yielded pure 4-*keto*-2-*methyltetrahydro*-1 : 5-*heptabenzthiazine* in small, granular, colourless plates (2 g.), m. p. 205—206° (Found: C, 61·9; H, 5·6. $C_{10}H_{11}ONS$ requires C, 62·2; H, 5·7%).

The compound is soluble in glacial acetic acid, benzene, or ligroin, and sparingly soluble in ether. It crystallises from chloroform in thin needles.

The *acetyl* derivative (XVI; R = Me) was obtained by boiling the substance with excess of acetic anhydride for 10 minutes, and separated from dilute alcohol in thin, colourless, glistening needles, m. p. 93° (Found: C, 60·9; H, 5·5. $C_{12}H_{13}O_2NS$ requires C, 61·3; H, 5·5%). It is readily hydrolysed by warming on the water-bath with dilute hydrochloric acid or sodium carbonate for a short time,

giving the original material (m. p. 205—206°). It is moderately easily soluble in alcohol and readily soluble in ether.

IV. *Acrylic Acid and* o-*Aminothiophenol.*

4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine* (IX).—Acrylic acid (2 g.) and *o*-aminothiophenol (3·5 g.) were heated together in an atmosphere of carbon dioxide at 125—130° for about an hour. The crystalline product was washed with ether and recrystallised from dilute alcohol, from which 4-*ketotetrahydro*-1 : 5-*heptabenzthiazine* separated in small, lustrous, colourless needles (1·3 g.), m. p. 215—216° (Found: C, 60·5; H, 5·1. C_9H_9ONS requires C, 60·3; H, 5·0%). The compound is readily soluble in acetone or glacial acetic acid, sparingly soluble in benzene, and practically insoluble in ether, chloroform, or light petroleum.

The *acetyl* derivative (XVI; R = H) was obtained by boiling the compound with excess of acetic anhydride for 15 minutes. It crystallised from alcohol in small, colourless needles, m. p. 96—97° (Found: C, 59·8; H, 5·0; N, 6·3; S, 14·4. $C_{11}H_{11}O_2NS$ requires C, 59·7; H, 5·0; N, 6·3; S, 14·5%). It is hydrolysed by warm dilute hydrochloric acid, yielding the original material.

Synthesis of 4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine* (IX) *from Acrylic Acid and* o-*Nitrothiophenol.*—The *o*-nitrothiophenol was obtained by reduction of *oo'*-dinitrodiphenyl disulphide by means of sodium sulphide (Claasz, *Ber.*, 1912, **45**, 747) and isolated from the solution by means of dilute acetic acid. It crystallised from light petroleum in pale yellow needles, m. p. 61°.

Addition of o-*nitrothiophenol to acrylic acid:* o-*Nitrophenylthiolpropionic acid* (XI). *o*-Nitrothiophenol (5·2 g.) and acrylic acid (2·4 g.) were together dissolved in dry benzene (25 c.c.) with the addition of 2—3 drops of piperidine, and the solution kept for 48 hours (compare Ruhemann, J., 1905, **87**, 17); o-*nitrophenylthiolpropionic acid* gradually separated in yellow crystals. Recrystallised from glacial acetic acid, it formed short, yellow needles (4 g.), m. p. 148—149° (Found: C, 47·7; H, 4·0. $C_9H_9O_4NS$ requires C, 47·6; H, 4·0%).

o-*Aminophenylthiolpropionic acid* (X). A mixture of *o*-nitrophenylthiolpropionic acid (4·5 g.), concentrated hydrochloric acid (15 g.), and tin (7·1 g.) was heated on the water-bath until the reduction was complete. The solution was then largely diluted with water, treated with hydrogen sulphide to precipitate the tin, and concentrated by evaporation in a vacuum. On cooling, the hydrochloride of *o*-aminophenylthiolpropionic acid separated in short, colourless needles, m. p. 173—174°, which soon became coloured on standing.

On treating the hydrochloride (1·2 g.) in concentrated aqueous solution with *N*-sodium hydroxide (5 c.c.), the *amino-acid* was obtained in colourless crystals (0·8 g.), which separated from dilute alcohol in short, thick needles, m. p. 87—88° (Found: C, 54·8; H, 5·7. $C_9H_{11}O_2NS$ requires C, 54·8; H, 5·6%) (compare Mayer and Horst, *loc. cit.*).

4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine*. The hydrochloride of *o*-aminophenylthiolpropionic acid (1·5 g.) was heated at 180—190° for ½ hour, hydrogen chloride and water being eliminated. On cooling, the product set to a reddish-brown solid, which, crystallised from alcohol, yielded pure ketotetrahydro-1 : 5-heptabenzthiazine (0·2 g.) in lustrous, colourless needles, m. p. and "mixed m. p." with the lactam synthesised from acrylic acid and *o*-aminothiophenol, 215—216°.

The acetyl derivative of the lactam was obtained on heating the above hydrochloride with excess of acetic anhydride for 30 minutes.

V. *Maleic Acid and* o-*Aminothiophenol.*

3-*Keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*acetic Acid* (XIV).—Maleic acid (3·5 g.) and *o*-aminothiophenol (3 g.), when mixed, reacted readily with considerable development of heat and the whole soon set to a hard mass. After being heated for a few minutes at 100—110°, the product was crystallised from dilute alcohol, from which it separated in small, colourless needles, melting at 195—196°, and at the same temperature after mixture with pure 3-*keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*acetic acid* synthesised from *o*-aminothiophenol and monobromosuccinic acid (see below). Yield 5 g. (93·5%) (Found: C, 53·6; H, 4·0. $C_{10}H_9O_3NS$ requires C, 53·8; H, 4·0%).

The compound is soluble in alcohol, sparingly soluble in ether, and practically insoluble in benzene, chloroform, or ligroin. It crystallises from water in thin, silky needles. It dissolves readily in cold, dilute sodium carbonate solution and is precipitated on acidification. After boiling for some time with 10% caustic potash solution it was precipitated unchanged on acidification.

The same product was obtained from fumaric acid and *o*-aminothiophenol. In this case no reaction appeared to take place in the cold, but the compound was readily formed on heating the two substances together at 150—160° for 15 minutes.

3-*Keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*acetic Acid from Monobromosuccinic Acid*.—Monobromosuccinic acid (1 g.) and *o*-aminothiophenol (0·6 g.) were heated together in an atmosphere of carbon dioxide at 120—125° for 15 minutes; a vigorous reaction then occurred and the mixture soon set to a solid mass. The product

was crystallised twice from dilute alcohol (charcoal) and pure keto-dihydrobenzthiazineacetic acid was thus obtained in small, colourless needles (0·6 g.), m. p. 195—196° (Found : C, 54·2; H, 4·0%).

The following work was kindly carried out by Mr. G. E. WATTS :

Diacetyl Derivative of o-*Aminothioanisole.*—*o*-Aminothioanisole (10 g.) was boiled with acetic anhydride (30 g. ; 4 mols.) for an hour. The resulting solution was distilled in a vacuum to remove acetic acid and anhydride, and the residual gum crystallised from alcohol, from which the *diacetyl* derivative separated in colourless, transparent prisms, m. p. 69—70°. Yield, 13 g. (82%) (Found : C, 59·1; H, 5·9; N, 6·1. $C_{11}H_{13}O_2NS$ requires C, 59·2; H, 5·8; N, 6·3%).

Preparation of Benzthiazolone (XVIII).—*Ethyl* o-*nitrophenylthiolformate,* $NO_2 \cdot C_6H_4 \cdot S \cdot CO_2Et$. To a solution (deep red) of *o*-nitrothiophenol (31 g.) in alcoholic sodium hydroxide (8 g. of NaOH in 30 c.c. of alcohol) a solution of ethyl chloroformate (21·7 g.) in alcohol (20 c.c.) was added, with shaking; the red colour of the nitrothiophenol soon disappeared, considerable heat was evolved, and sodium chloride was precipitated. The mixture was poured into water (500 c.c.) and the ethyl nitrophenylthiolformate, which separated as a yellow oil, was extracted with ether. It decomposed when heated in a vacuum.

Ethyl o-*aminophenylthiolformate.* Crude ethyl nitrophenylthiolformate (35 g.), mixed with alcohol (20 c.c.), was shaken with a solution of stannous chloride (115 g.) in concentrated hydrochloric acid (50 c.c.) for an hour, the mixture being cooled in ice from time to time. The solution was diluted, freed from tin by means of hydrogen sulphide, made alkaline with sodium bicarbonate, and extracted with ether. On removal of the ether the amino-ester remained as a colourless oil. Yield, 20 g. (67%).

The *hydrochloride* of the amino-ester was prepared by treating an alcoholic solution of the ester with hydrogen chloride and precipitated by the addition of ether. It crystallised from alcohol–ether in fine, colourless needles, m. p. 120—122° (Found : Cl, 15·2. $C_9H_{12}O_2NClS$ requires Cl, 15·2%).

Benzthiazolone. Ethyl *o*-aminophenylthiolformate, mixed with a little of its hydrochloride, was heated at 115° for 2 hours; it then changed to a crystalline mass. This, recrystallised from aqueous alcohol, gave colourless needles of benzthiazolone; they melted at 128° and were readily soluble in strong alkalis and in strong mineral acids (compare Claasz, *Ber.*, 1912, **45**, 1029).

The acetyl derivative was obtained by boiling the substance with excess of acetic anhydride for 15 minutes. It separated from aqueous alcohol in fine, colourless needles, m. p. 50° (compare Claasz,

loc. cit.), and was readily hydrolysed by warm 10% sodium hydroxide solution, giving the original material.

One of us (J. B. W.) wishes to express his indebtedness to the Chemical Society for a grant which defrayed part of the cost of this investigation.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, August 25th,* 1927.]

CCCLXVI.—*Organic Compounds of Arsenic. Part III. Tri-o-phenylenediarsine.*

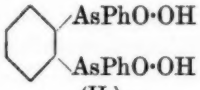
By NIAL PATRICK MCCLELAND and JAMES BELL WHITWORTH.

TRI-*o*-PHENYLENEDIARSINE (I) appears to be the first compound in which it is established that a pair of atoms is linked to each of three benzene rings in the ortho-position in such a way that, a symmetrical grouping being assumed, the planes of the rings are inclined at 120° to one another.

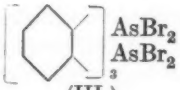
A substance, $C_{18}H_{12}N_2$, described in the literature as triphenylenediamine was obtained by von Dechend and Wichelhaus (*Ber.*, 1875, **8**, 1609) by the action of nitrobenzene on aniline or diphenylamine, but its constitution is unknown.

The new substance (I) was obtained as follows: Diazotised *o*-aminodiphenylarsinic acid coupled with phenylarsine oxide to give *phenylene*-1 : 2-*diphenylarsinic acid* (II), which was then reduced with phosphorus trichloride, presumably to phenylene-1 : 2-diphenylchloroarsine; this was not obtained in the pure state and on distillation it gave *tri*-o-*phenylenediarsine* (I), evidently by the loss of two molecules of hydrogen chloride and consequent double ring closure.

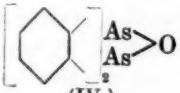
(I.)



(II.)



(III.)



(IV.)

The constitution of the substance (I) is supported by the following observations, which show that triphenylenediarsine bears the same relation to the derivatives of arsanthrene (Kalb, *Annalen*, 1921, **423**, 39) as the triarylarsines do to those of the diarylarsines: (1) as triphenylarsine dichloride decomposes on distillation into diphenylchloroarsine and chlorobenzene (La Coste and Michaelis, *Annalen*, 1880, **201**, 242; Michaelis, *ibid.*, 1902, **321**, 142, 160; Winmill, J., 1912, **101**, 720), so triphenylenediarsine tetrabromide (III) on

heating gives (in addition to bromine and triphenylenediarsine) *o*-dibromobenzene and arsanthrene bromide; (2) as di-*p*-tolylarsenious oxide on heating gives tri-*p*-tolylarsine (La Coste, *Annalen*, 1881, **208**, 20), so arsanthrene oxide (IV) on distillation gives triphenylenediarsine and arsenious oxide as indicated by the equation 3 (IV) = 2 (I) + As_2O_3 (compare the decomposition of phenylarsine oxide into triphenylarsine and arsenious oxide on heating; La Coste and Michaelis, *ibid.*, p. 239).

Moreover, the substance behaves as a tertiary arsine, being converted into the oxide by nitric acid and forming a tetrabromide and a mercurichloride.

Triphenylenediarsine is formed in the preparation of arsanthrene chloride by Kalb's method (*loc. cit.*) and probably accounts for the sparingly soluble impurity which he found in arsanthrene oxide.

The stereochemistry of the new system is under investigation, and it is hoped to prepare corresponding compounds with other elements in place of arsenic.

Experimental.

Phenylene-1 : 2-*diphenylarsinic Acid* (II).—Into a well-stirred, diazotised solution of *o*-aminodiphenylarsinic acid (20 g.; concentrated hydrochloric acid, 58 c.c.; water, 700 c.c.; ice, 500 g.) was run a solution of phenyldichloroarsine (18 g.) in 5*N*-caustic soda (64 c.c.) to which sodium acetate (58 g.), dissolved in ice-water (450 c.c.), had been added just previously. The mixture was made alkaline with caustic soda, boiled with charcoal, and filtered. On acidification, the filtrate gave a yellowish-brown, pasty precipitate. This was boiled with alcohol, which removed most of the coloured impurity, the residue was dissolved in a large volume of dilute aqueous ammonia, the solution neutralised with acetic acid and boiled with charcoal, and an excess of dilute acetic acid added to the boiling filtered solution; *phenylene*-1 : 2-*diphenylarsinic acid* (9 g.) then slowly separated in pale yellow, microscopic crystals which did not melt below 310° and were insoluble in water and in the usual organic solvents (Found: C, 49·0; H, 3·5. $C_{18}H_{16}O_4As_2$ requires C, 48·4; H, 3·6%).

Tri-o-*phenylenediarsine* (I).—Phenylene-1 : 2-diphenylarsinic acid (9 g.), suspended in chloroform (100 c.c.), was treated with excess of phosphorus trichloride (25 g.), heat being evolved and most of the acid dissolving. The solution was heated on the water-bath for 3 hours and filtered from a little tar. On distillation of the solvent a dark brown, oily residue was obtained from which no crystalline product could be isolated. It was therefore heated under reduced pressure; vigorous frothing occurred at 120—300°,

and at 320—340°, crystals of *triphenylenediarsine* gradually sublimed on the upper part of the distilling flask, but no distillate was obtained. The crystalline product was collected and a further quantity was obtained on extracting the charred residue in the flask with hot benzene. On recrystallisation from benzene (charcoal), triphenylenediarsine (2·5 g.) was obtained in small, almost colourless plates, m. p. 295—296°. It is soluble in benzene, acetone, or light petroleum, readily soluble in chloroform, sparingly soluble in alcohol or ether, and insoluble in water. It can be sublimed without decomposition (Found: C, 57·4; H, 3·2; As, 40·1; *M*, in camphor by Rast's method, 360, 396, 364. $C_{18}H_{12}As_2$ requires C, 57·1; H, 3·2; As, 39·8%; *M*, 378).

The authors are indebted to Professor Hutchinson for the determination of the crystallographic constants:

System: Monoclinic (holohedral). $a : b : c = 1{\cdot}589 : 1 : -$; $\beta = 113°\ 15'$. Forms present: *a*(100), *c*(001), *m*(110). Angles observed: *am* 55° 35′, *ac* 66° 45′.

The crystals are elongated parallel to the axis of the zone [*am*] and are either tabular parallel to *a* with *m* and *c* small or bounded by *m* and *c* planes with *a* small or absent. The face *c* is invariably somewhat rounded. The optic axial plane is perpendicular to the plane of symmetry and lies in the obtuse axial angle. A negative acute bisectrix emerges obliquely from *a*. On viewing the crystal in monochromatic convergent light perpendicular to a pair of *m* faces, the emergence of an optic axis near the edge of the field can be seen. In white light, the dark brush passing through the centre of the ring system is replaced by brilliant red and blue fringes, indicating strong dispersion, and no extinction can be obtained on the *m* face in parallel light. The material available did not lend itself to an accurate determination of the optical constants, but β for sodium light was found to be 1·790 approximately.

The *mercurichloride* was obtained in short, colourless needles from the diarsine and mercuric chloride in cold acetone; after recrystallisation from alcohol, in which it was sparingly soluble, it melted at 285—286°. It was readily decomposed by warm dilute caustic soda solution.

The *oxide* was obtained on boiling the diarsine with concentrated nitric acid and pouring the resulting solution into water. It was readily soluble in alcohol and separated from dilute aqueous alcohol in short, thin, colourless needles, which did not melt below 360° (Found: C, 52·6; H, 3·0. $C_{18}H_{12}O_2As_2$ requires C, 52·7; H, 2·9%).

The *tetrabromide* (III) was precipitated as an orange-red, crystalline substance, m. p. 255—256°, when the diarsine was treated with a small excess of bromine in dry chloroform (Found: Br, 45·7.

$C_{18}H_{12}Br_4As_2$ requires Br, 45·9%). It is readily soluble in acetone or alcohol and in hot glacial acetic acid (with decomp.), sparingly soluble in chloroform, and insoluble in ether, benzene, or light petroleum. It is readily decomposed by dilute caustic soda solution or even by water, giving the colourless oxide (Found: As, 36·4. Calc. for $C_{18}H_{12}O_2As_2$: As, 36·7%).

When the tetrabromide was heated under reduced pressure (15 mm.), decomposition took place at about 260°, much bromine was evolved, and a small quantity of a yellow liquid distilled; the residue set to a crystalline mass on cooling. The liquid product was dissolved in ether, treated with caustic soda to remove free bromine, and distilled in a vacuum, being thus obtained as a colourless oil, b. p. 104—105°/15 mm., 224°/ordinary pressure (Found: Br, 68·2. Calc. for $C_6H_4Br_2$: Br, 67·8%). On intensive cooling, the liquid set to a colourless solid, m. p. 4°. It was concluded that the liquid was *o*-dibromobenzene, which has b. p. 224° and m. p. 5·6°. (The *m*-isomeride has b. p. 220° and m. p. — 7°, and the *p*-isomeride, m. p. 87°.)

As it would probably have been difficult to separate the small amount of arsanthrene bromide from the triphenylenediarsine by recrystallisation, the crystalline residue was treated with alcoholic ammonia to convert the arsanthrene bromide into the oxide. After dilution with water, the product was collected and extracted with hot alcohol, the portion remaining undissolved consisting of triphenylenediarsine, which after recrystallisation from benzene gave m. p. and "mixed m. p." 295—296°. The cooled alcoholic extract was filtered from a small amount of the diarsine which had separated and was then concentrated. Arsanthrene oxide, which separated on cooling, crystallised from alcohol in small, lustrous plates which, alone or mixed with pure arsanthrene oxide, melted at 194—195°.

The presence of bromide in the ammoniacal liquor was verified.

Treatment of triphenylenediarsine with chlorine yielded a light yellow compound, which has not been investigated. Methyl iodide gave no addition compound on prolonged heating with the diarsine in a sealed tube at 50—60°.

Formation of Triphenylenediarsine from Arsanthrene Oxide.—Pure arsanthrene oxide distilled under 15 mm. pressure, without appreciable decomposition, as a yellow liquid, which rapidly solidified. When, however, the pure oxide was distilled in a current of carbon dioxide under only slightly reduced pressure, considerable decomposition took place. Arsenious oxide sublimed into the receiver, and a crystalline substance on the upper part of the distilling flask. The crystalline product was extracted with hot alcohol to remove any unchanged oxide and then recrystallised from

benzene, from which it separated in small, colourless plates, m. p. 295—296°, and at the same temperature after mixture with pure triphenylenediarsine. The dark brown residue in the distilling flask gave a further small quantity of the diarsine on extraction with benzene.

Triphenylenediarsine appears to be formed during the distillation of arsanthrene chloride, for, when arsanthrene chloride prepared by Kalb's method (*loc. cit.*) was converted into the oxide by alcoholic ammonia, and the oxide crystallised from alcohol, a small quantity of triphenylenediarsine remained undissolved. It separated from benzene in small, colourless plates, m. p. and " mixed m. p. " with the pure diarsine 295—296° (Found : C, 57·3; H, 3·1%), and on oxidation with nitric acid it gave triphenylenediarsine oxide as fine needles (Found : C, 52·7; H, 2·8%).

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CCCLXVII.—*The Halogenation of Phenols. Part II. Iodination.*

By FREDERICK GEORGE SOPER and GILBERT FREEMAN SMITH.

THE relative ionisation constants of chlorine and hypochlorous acid to give a positive halogen ion (Soper and Smith, J., 1926, 1582) express qualitatively the ease with which these substances chlorinate phenols. A study of the chlorination by hypochlorous acid showed, however, that the hypochlorous acid *molecule* was the chlorinating agent, so that the parallelism between the ease of chlorination and the ionisation constant of the chlorinating molecule is not due to preliminary ionisation into a reactive positive halogen ion. The ionisation constant of the halogenating agent may be regarded as a measure of the number of polarised molecules present and collisions between these and other molecules may be effective. It was of interest to extend this line of argument to iodination by iodine and by hypoiodous acid, the relative ionisation constants of which, given by the ratio K_h/K_w (K_h being the hydrolysis constant, $C_H \cdot C_I / C_{HOI}/C_{I_2} = 3 \times 10^{-13}$, of iodine in water; Bray and Connolly, *J. Amer. Chem. Soc.*, 1911, **33**, 1485), are as 30 to 1. It might be expected from this ratio that the ease of halogenation by iodine would be comparable with that by hypoiodous acid.

The mechanism of the iodination of phenols was investigated by Cofman (J., 1919, **115**, 1040), who showed that in acid solution iodine does not iodinate, whilst the active iodine in an alkaline

solution was equal to the concentration of hypoiodous acid, as calculated from the known kinetics of iodate formation (Skrabal, *Monatsh.*, 1911, **32**, 171). It might appear from these facts that iodine is incapable of iodination and that hypoiodous acid or (as Cofman suggests as an alternative) the positive iodine ion is the halogenating agent. As, however, in acid solution the phenol would be mainly un-ionised, whilst in alkaline solution the very much more highly reactive phenoxide ions would be present, the mechanism has been further examined in order to determine whether iodine is capable of reacting with phenoxide ions.

Examination of the speed of iodination of phenol was carried out by the use of a solution of iodine in potassium iodide in the presence of a neutral phosphate buffer. If molecular iodine is involved in the interaction, then the speed will be proportional, on the classical reaction-velocity equation, to the concentration of free iodine in the mixture. The equilibrium concentration of free iodine can be calculated from the expression $C_{I_2}C_{I'}/C_{I_3'} = K_1$ (Bray and MacKay, *J. Amer. Chem. Soc.*, 1910, **32**, 914), using the appropriate value for K_1 which depends on the iodide concentration. The speed of iodination at constant phenol concentration will thus be given by $v = k_{I_2}K_1C_{I_3'}/C_{I'}$, and since, in the presence of excess of iodide ions, $C_{I_3'}$ is represented sufficiently accurately by the thiosulphate titre of the solution, the velocity coefficient, k_1, of the reaction calculated from the equation

$$v = k_1 \times \text{thiosulphate titre} \quad . \quad . \quad . \quad . \quad (1)$$

should vary inversely as the iodide-ion concentration.

If the iodination is caused by hypoiodous acid, the velocity coefficient k_1 should vary approximately as the inverse of the square of the concentration of the iodide ion at constant hydrogen-ion concentration, for $C_{HOI}a_H.a_{I'}/C_{I_2} = K_h = 3 \times 10^{-13}$, a denoting the appropriate activity * of the ion, and hence

$$v = k_{HOI} \,.\, C_{HOI} = k_{HOI}K_hK_1C_{I_3'}/a_H.a_{I'}C_{I'} \quad . \quad . \quad . \quad (2)$$

The results obtained are given in Table I. The values of the activity of the iodide ion, $a_{I'}$, have been interpolated for the appropriate ionic strength, μ, from a table of the activities of the chloride ion (Lewis and Randall, "Thermodynamics," 1924, p. 351). The concentrations of iodine and of hypoiodous acid given in cols. 4 and 6, respectively, are the initial equilibrium concentrations of these substances in the reaction mixture. The unimolecular coefficient k_1 (the mean of two experiments agreeing to within 1%) is seen to

* The activity of a neutral molecule has been equated to its concentration, in the absence of other information.

be proportional to the initial concentration of the hypoiodous acid. Although the concentration of the iodine is between 10^4 and 10^5 times that of the hypoiodous acid, there is no appreciable iodination by iodine.

TABLE I.

Ph·OH = 0·010; I_2 added = 0·001M; Temp. = 25·0°; $a_{H^+} = 10^{-7}$.

μ.	$C_{I'}$.	$K_1 . 10^3$.	$C_{I_2} . 10^5$.	$a_{I'}$.	$C_{HOI} . 10^{10}$.	k_1.	$10^{-4} . k_1 / C_{I_2}$.	$10^{-8} . k_1 / C_{HOI}$.
0·2092	0·1	1·31	1·295	0·0745	5·231	0·1926	1·486	3·685
0·3092	0·2	1·21	0·605	0·1434	1·287	0·0477	0·788	3·75
0·5092	0·4	1·00	0·250	0·2724	0·2752	0·0102	0·407	3·71

It is now necessary to differentiate between the interaction of hypoiodous acid and that of positive iodine ion with the phenol molecule or with the phenoxide ion. This is possible by an examination of the speed of iodination in solutions containing a constant concentration of iodide ion and various hydrogen-ion concentrations. Since the reaction is examined over the hydrogen-ion concentration range from $0·5 \times 10^{-7}$ to 4×10^{-7}, the phenol exists mainly in the un-ionised condition, its ionisation constant, K_a, being $1·1 \times 10^{-10}$. The concentration of phenoxide ions is thus inversely proportional to the hydrogen-ion concentration.

For a reaction between hypoiodous acid and phenol, the speed will be given by

$$v = k_2 C_{HOI} C_{Ph·OH} = k_2 K_1 K_h C_{Ph·OH} C_{I_2'} / a_{H^+} a_{I'} C_{I'}$$
$$= k_2 K_I K_h C_{Ph·OH} C_{I_2'} / a_{H^+} f_{I'} C_{I'}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $f_{I'}$ is the activity coefficient of the iodide ion. The velocity coefficient, k_1, of equation (1) should vary inversely as $f_{I'} a_{H^+}$, or, since the ionic strength is nearly constant in the different mixtures, inversely as the hydrogen-ion activity. If the reaction is between the phenoxide *ion* and hypoiodous acid,

$$v = k_3 C_{HOI} C_{Ph·O'}$$
$$= k_3 K_1 K_h K_a C_{Ph·OH} C_{I_2'} / a_{H^+}{}^2 f_{Ph·O'} f_{I'} C_{I'}^2 \quad . \quad . \quad (4)$$

and k_1 should vary approximately as the inverse of the square of the hydrogen-ion activity.

For iodination by positive iodine ions, the concentration of which is controlled by the equilibrium constant $K_2 = a_{I'} a_{I'} / C_{I_2} = a_{I'} C_{I'} f_{I'} / C_{I_2}$, the velocity equation will be $v = k_4 C_{Ph·OH} C_{I'} = k_4 K_1 K_2 C_{Ph·OH} C_{I_2'} / C_{I'} a_{I'} f_{I'}$, and k_1 would be independent of the hydrogen-ion concentration, whilst for an interaction of positive iodine ion with the phenoxide ion the constant k_1 would be inversely proportional (approximately) to the hydrogen-ion concentration. Actually, experiments carried out at the hydrogen-ion

activities of 0·5, 1·0, 2·0, and $3·98 \times 10^{-7}$ showed that the velocity coefficient k_1 varied more rapidly than the inverse of the hydrogen-ion activity of the mixture, but less rapidly than its inverse square. The results are summarised in Table II.

TABLE II.

Ph·OH = 0·010; KI = 0·100; temp. = 25·0°.

HPO_4''.	H_2PO_4'.	μ.	$f_{I'}$.	$a_{H^+} . 10^7$.	k_1 (obs.).	$10^7 \times k_1 a_{H^+}$.	$10^{14} \times k_1 a_{H^+}^2$.	k_1 (calc.).
0·0370	0·0130	0·224	0·741	0·5	0·420	0·210	0·105	0·440
0·0296	0·02037	0·209	0·745	1·0	0·193	0·198	0·193	0·182
0·0205	0·0295	0·191	0·752	2·0	0·083	0·166	0·322	0·081
0·0126	0·0374	0·175	0·759	3·98	0·036	0·143	0·570	0·038

Assigning the values $4·85 \times 10^9$ and $2·76 \times 10^7$ to k_3 and k_2 respectively, and taking the value of $f_{Ph·O'}$ as equal to that of $f_{I'}$, k_1 has been calculated from the equation

$$v = k_2 C_{HOI} C_{Ph·OH} + k_3 C_{HOI} C_{Ph·O'}$$
$$= \frac{K_1 K_h C_{Ph·OH} C_{I_2'}}{a_{H^+} C_{I'}^2 f_{I'}} (k_2 + k_3 K_a / a_{H^+} f_{Ph·O'}) \quad . \quad . \quad . \quad (5)$$

which, in combination with (1), gives

$$k_1 = \frac{K_1 K_h C_{Ph·OH}}{a_{H^+} C_{I'}^2 f_{I'}} (k_2 + k_3 K_a / a_{H^+} f_{Ph·O'}) \quad . \quad . \quad . \quad (6)$$

Bearing in mind the necessarily approximate values used for the activities of the various ions and neutral molecules, the divergencies between the observed and calculated values of k_1 are not unreasonable.

Conclusions.

It would thus appear that the iodination of phenol is not caused by the positive iodine ion, but that the main reactions are those between the hypoiodous acid and the ionised and un-ionised phenol, the reactivity of the phenoxide ion being 180 times that of the phenol molecule. Molecular iodine is a singularly poor iodinating agent, being at least 10^6 times less active than hypoiodous acid in spite of its greater ease of ionisation and, presumably, its more highly polar condition.

The behaviour of halogens and the hypohalous acids towards phenols (as illustrated by chlorine and iodine) is thus not entirely explained on a theory of reactivity governed by the polar state of the molecules, iodination indicating that some other factor can dominate. This factor may be the affinity of the residual nuclear hydrogen for the residue of the halogenating molecule. The affinity of the hydrogen ion for the hydroxyl ion is so much greater than for the iodide ion that hypoiodous acid becomes very much

more reactive than iodine. In chlorination, however, the large difference in the affinities of Cl' for OH' and for Cl' ($4{\cdot}8 \times 10^{10}$ to 1) appears to be the controlling factor.

EXPERIMENTAL.

Buffer Solutions.—The phosphate buffer solutions were prepared from potassium dihydrogen phosphate (B.D.H., A.R.) and sodium hydroxide free from carbonate; the quantities taken (Table II) were interpolated from those given by Clark ("Determination of Hydrogen Ions," N.Y., 1920, p. 76). Conductivity water was used in making up all the solutions.

Measurement of the Speed of Iodination.—The reaction was started by addition of the iodine solution in potassium iodide to the mixture of phenol (m. p. 40·0°) and phosphate buffer solution at 25·0°. 10 C.c. of the reaction mixture were removed at suitable intervals and run into 50 c.c. of 0·5*N*-sulphuric acid, whereby the reaction was stopped. Titration of the residual iodine with *N*/500-thiosulphate was carried out in an atmosphere of nitrogen, which enabled perfectly sharp end-points to be obtained. The results for a typical experiment are given in Table III.

TABLE III.

0·05*M*-KH_2PO_4; 0·0296*M*-NaOH; 0·01*M*-Ph·OH; 0·001*M*-I_2; temp. 25·0° ± 0·02°.

Time (mins.) .	0	8·70	13·97	22·80	35·58	49·90	64·93
$[I_2'] \times 10_4$ ...	9·67	8·07	7·27	5·98	4·60	3·48	2·56
$k_1/2{\cdot}303$	—	0·0208	0·0205	0·0210	0·0208	0·0205	0·0205

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CCCLXVIII.—*The Activity Theory of Reaction Velocity. The Interaction of* N*-Chloroacetanilide and Hydrochloric Acid.*

By FREDERICK GEORGE SOPER and DAVID REGINALD PRYDE.

THE effect of electrolytes on the speed of reactions catalysed by acids is interpreted at the present time along two lines. On one theory, the catalyst is the hydrogen ion, its catalytic activity being proportional either to its thermodynamic activity (Harned, *J. Amer. Chem. Soc.*, 1918, **40**, 1461), which is affected by the presence of salts, or to its concentration (Brönsted and Pedersen, *Z. physikal. Chem.*, 1924, **108**, 185) as calculated from the concentration ionisation constant, which changes with the ionic strength (Arrhenius,

Z. physikal. Chem., 1899, **31**, 197; Brönsted, J., 1921, **119**, 574). The other theory, which has recently been extended by Dawson (Dawson and Carter, J., 1926, 2282 *et seq.*), attributes catalytic activities to the undissociated molecule and to the acid anion, as well as to the hydrogen ion. On the latter theory, the catalytic activities of the various ions are assumed to be proportional to their concentrations. It may be noted, however, that Dawson, in calculating his hydrogen-ion concentrations in acetic acid–acetate mixtures, uses a constant value for the ionisation constant of acetic acid in which he substitutes for the acid and anion concentrations (Dawson and Dean, *ibid.*, p. 2876); no allowance is made for the increase of the concentration ionisation constant (some 200%: Brönsted, *loc. cit.*; compare K_w, Harned, *J. Amer. Chem. Soc.*, 1925, **47**, 930) as the salt concentration is increased from 0 to 1·0*N*.

A factor very generally neglected in the study of acid catalysis is the effect the electrolyte may have on the active mass of the non-electrolyte, as demonstrated by the experiments of Jones and Lapworth (J., 1911, **99**, 1427), who found that the equilibrium constant of the reaction $EtOH + CH_3{\cdot}CO_2H \rightleftharpoons CH_3{\cdot}CO_2Et + H_2O$ changes by more than 100% as the amount of the catalyst, hydrogen chloride, is altered. Since the catalyst does not appear in the equilibrium constant, the velocity coefficients k and k' in the equations, $v = kC_{catalyst}C_{alcohol}C_{acid}$ and $v' = k'C_{catalyst}C_{ester}C_{water}$, must vary as the catalyst concentration changes. The general procedure has been to regard k as strictly constant, and to deduce the effective concentration of the catalyst on this assumption. It is obvious that this procedure may lead to erroneous theories. If deductions are to be made as to the effective concentrations of the catalyst, k, and therefore k/k', must be strictly constant. The equilibrium constant of a system must therefore be expressed in such a way as to be independent of the changes in medium caused by the addition of neutral salts, and the velocity equation must be modified so as to be in harmony with this equilibrium constant. An equilibrium constant of this nature was proposed by van 't Hoff (Lectures, 1898), concentrations being replaced by the ratio of concentration to the limiting solubility in the particular medium. Replacement of concentrations by this ratio in the velocity equation $v = kC$ gives $v = k_0C/S$; Dimroth (*Annalen*, 1910, **377**, 127) used this equation in studying the effects of solvents on the velocity of intramolecular transformation, and found that, whilst the classical velocity coefficient had values which differed as much as 100-fold from each other, the values of k_0 only exhibited a 3-fold variation. It would thus appear that part of the effect of the medium on

reaction speed is connected with solubility. It follows that, if the solubility of a non-electrolyte, such as ethyl acetate, is decreased by the presence of electrolytes, its reactivity may be increased. This is also indicated from a consideration of the kinetic equilibrium of a solid with its saturated solution. If the solubility is decreased, a greater proportion of the solute molecules must possess sufficient translational energy to deposit themselves on the surface of the solid, and the reactivity, which depends on the proportion of molecules having an energy greater than some critical value (Arrhenius, *Z. physikal. Chem.*, 1889, **4**, 226; Hinshelwood, *Phil. Mag.*, 1925, **2**, 360), may be expected to increase (Scatchard, *J. Amer. Chem. Soc.*, 1923, **45**, 1581).

The van 't Hoff equilibrium constant is a partial statement of the activity constant. Defining the activity, a_A, of a substance A by the expression $F_A = C_A + RT \log a_A$, where F_A is the partial free energy and C_A is a constant, and putting $F_A + F_B = F_P + F_Q$ as the condition * of equilibrium in the system $A + B \rightleftharpoons P + Q$, it is seen that $a_A a_B / a_P a_Q$ is constant and independent of the medium. The modified velocity equation corresponding to the classical equation is thus $v = k a_A a_B$, but it is important to note that this equation is only one of a number which, when applied to a balanced reaction, satisfy the activity equilibrium constant. The general velocity equation is of the type

$$v = k_0 a_A a_B F_1 \text{ (activities)}. \quad F_2 \text{ (specific effect of solvent)}. \quad F_3 \ldots F_n, \ldots \ldots \ldots \ldots \ldots \quad (1)$$

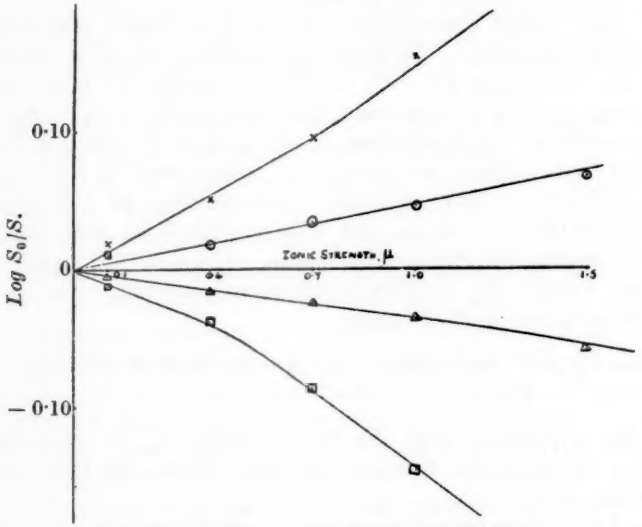
with the stipulation that the functions F_1, F_2 . . ., should be common to both the forward and the reverse reactions of the reversible change.

The object of the present work was to test the equation $v = k a_A a_B$, or, if this was inadequate, some equation of the general type (1), and for this purpose a knowledge of the activities of the reacting substances in the presence of each other is necessary. Whilst the effect of small concentrations of a non-electrolyte on the activity of an electrolyte is negligible, the electrolyte may exert a large effect on that of the non-electrolyte. The determination of the activity of a substance in the presence of those reagents which are causing its decomposition is difficult, and it does not suffice to regard the salting-out effect of all electrolytes as identical at equivalent concentrations. It has been possible to overcome this difficulty in the study of the interaction of hydrochloric acid and *N*-chloroacetanilide (Orton and Jones, *Rep. Brit. Assoc.*, 1910,

* This is permissible if a displacement of the equilibrium is not attended by a change in the ionic strength (Soper, *J. Physical Chem.*, 1927, **31**, Nov.).

85; Rivett, *Z. physikal. Chem.*, 1913, **82**, 301; Harned and Seltz, *J. Amer. Chem. Soc.*, 1922, **44**, 1475), for both hydrogen and chlorine ions must be present before the *N*-chloroacetanilide reacts, and it was therefore possible to measure separately the effects of these ions on the activity of the chloroamine. It was found that the replacement of the chloride ion by the nitrate ion raised the solubility of the chloroamine in a certain ratio, which depended on the salt concentration, but was otherwise independent of the kation present. From the solubility in nitric acid, that in hydrochloric acid could be deduced, and the activity coefficient was found in

FIG. 1.



△ HCl, ⊡ HNO_3, × KCl, ⊙ KNO_3 *solutions.*

this way to change by 13% over the hydrochloric acid range examined (0·1—1·5*M*). The results are given graphically in Fig. 1, where the logarithm of the activity coefficient of the chloroamine (the ratio of the solubility in water to that in the salt solution) has been plotted against the ionic strength.

Measurement of the Rate of Interaction of Hydrochloric Acid and N-*Chloroacetanilide.*—The transformation of *N*-chloroacetanilide to *o*- and *p*-chloroacetanilides was shown by Orton and Jones (*loc. cit.*) to involve two successive stages: first, an interaction of the hydrochloric acid and the chloroamine with the production of chlorine, and secondly, reaction between the chlorine and the acetanilide. It has since been shown by one of us (*J. Physical Chem.*, 1927, **31**, 1192) that the speed of the transformation is

approximately equal to that of the first stage, but that the measurement of the rate of reaction is complicated by simultaneous *N*-chlorination of the chloroanilides which are produced. The effect of this was shown to be that the rates of the transformation as ordinarily measured indicate an apparent reactivity of the hydrochloric acid, which is too great in the more concentrated acid solutions. In order to measure the true rate at which chlorine is being formed, it is necessary to have present excess of some substance which is readily chlorinated and does not itself react with the hydrochloric acid or the chloroamine. Acetanilide, phenol, and *p*-cresol have been used for this purpose, and have given identical results.

It is possible that chlorine may be produced from a chloroamine by two mechanisms: (1) a direct interaction of hydrochloric acid and the chloroamine the rate of which it is desired to measure, and (2) a primary hydrolysis of the chloroamine to hypochlorous acid, followed by the rapid interaction of hydrochloric and hypochlorous acids, giving chlorine (k_2 at $25° = 1{\cdot}0 \times 10^6$; Soper and Smith, J., 1926, 1582). If (2) occurs appreciably, the rate of chlorine formation will be greater than the rate of interaction of the chloroamine and hydrochloric acid. In aqueous solution, the rate of hydrolysis of *N*-chloroacetanilide is very slow, for in the presence of phenols with which hypochlorous acid reacts rapidly, no detectable disappearance of the chloroamine occurred in 7 hours. In acid solution, the rate of hydrolysis becomes measurable. It is unaffected by the amount of phenol present, is proportional to the acid strength, and is practically the same for nitric, sulphuric, and perchloric acids of the same concentration. If the rate of hydrolysis is the same in hydrochloric acid as in other acids, it is approximately 6% of the rate of chlorine formation in 0·1*M*-hydrochloric acid and decreases to 0·4% in 1·5*M*-acid. The rates of chlorine formation corrected for the rate of hydrolysis of the chloroamine give the speeds of direct interaction of the chloroamine and hydrochloric acid.

Activity of the Hydrochloric Acid.—Since the general activity reaction-velocity equation has been developed from the free-energy condition for equilibrium, $F_A + F_B = F_P + F_Q$, which applies strictly only to those equilibria in which a slight displacement does not affect the ionic strength, it is necessary to examine the reaction $(HCl \rightleftharpoons H^{\cdot} + Cl') + {:}NCl \longrightarrow Cl_2 + {:}NH$, more closely. Although the chlorine does not remain in the system, but is immediately taken up by other substances which are present, the velocity equation must satisfy the equilibrium conditions which would be attained were the chlorine to remain free in the system. For a

slight displacement of the above equilibrium such that dn mols. of hydrogen chloride disappear, there is a disappearance of $2dn$ ions, with a consequent decrease in the free electrical energy of the medium (Soper, *loc. cit.*). This change in the free energy of the medium is independent of whether the un-ionised acid or the ions actually react with the chloroamine. The equilibrium condition is therefore

$$-dF_{\text{H}\cdot} - dF_{\text{Cl}'} - dF_{:\text{NCl}} + dF_{\text{Cl}_2} + dF_{:\text{NH}} - dF_{\text{medium}} = 0. \quad (2)$$

The interaction of hydrochloric acid and the chloroamine is apparently of the third order, but since it has the normal temperature coefficient (Harned and Seltz, *loc. cit.*), whilst a true termolecular reaction, involving the simultaneous collision of 3 molecules, has a temperature coefficient of nearly unity (Bodenstein, *Z. physikal. Chem.*, 1922, **100**, 68), it is probable that the reaction is one involving the un-ionised hydrogen chloride and the chloroamine. The partial free energy of the un-ionised hydrogen chloride is connected with those of the hydrogen and chlorine ions by the equation

$$-dF_{\text{HCl}} + dF_{\text{H}\cdot} + dF_{\text{Cl}'} + dF_{\text{medium}} = 0 \quad . \quad . \quad (3)$$

where the dF_{medium} corresponds to the increase in the electrical free energy of the medium due to the formation of $2dn$ ions.

Combining (2) and (3), we have

$$-dF_{\text{HCl}} - dF_{:\text{NCl}} + dF_{\text{Cl}_2} + dF_{:\text{NH}} = 0,$$

or

$$F_{\text{HCl}} + F_{:\text{NCl}} = F_{\text{Cl}_2} + F_{:\text{NH}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and substitution for $F_{\text{HCl}} = RT \log a_{\text{HCl}} + C_{\text{HCl}}$ etc., gives

$$a_{\text{HCl}}a_{:\text{NCl}}/a_{\text{Cl}_2}a_{:\text{NH}} = \text{constant},$$

corresponding to the simple activity reaction-velocity equation

$$v^* = -dc_{:\text{NCl}}/dt = k_0 a_{\text{HCl}} a_{:\text{NCl}} = k_0 a_{\text{HCl}} f_{:\text{NCl}} c_{:\text{NCl}}. \quad . \quad . \quad . \quad (5)$$

Values of a_{HCl} are given by *E.M.F.* measurements on hydrochloric acid concentration cells without liquid junction, for in a slight displacement of the system in equilibrium the electrical work $dnE\text{F}/N$ is balanced by the change in the partial free energy of

* The speed is regarded as the number of g.-mols. of the reagents reacting in unit time *per unit volume*, rather than the number reacting per unit weight of solution, for the activity is connected, as was pointed out by Scatchard (*loc. cit.*), with the number of molecules possessing a certain critical energy which enables them to pass through, or react with, unit area of the boundary surface in unit time. If one imagines a number of planes of unit area immersed in the solution, then those molecules possessing sufficient energy to carry them through the surface will also pass through each of these planes. If the planes are of infinitesimal thickness and are arranged so as to form a solid cube, the activity will measure the number of molecules possessing a certain critical energy in that cube, *i.e.*, in unit volume. The number of molecules reacting should also, therefore, have reference to unit volume.

the hydrochloric acid caused by its transference from cell to cell together with the net change in the electrical energy of the two media, *i.e.*,

$$dnEF/N = -dF_{H\cdot I} - dF_{Cl'I} - dF_{\text{medium I}} + dF_{H\cdot II} + dF_{Cl'II} + dF_{\text{medium II}}$$

which, on being combined with (3), gives

$$dnEF/N = -dF_{HCl_I} + dF_{HCl_{II}}$$

and $EF = RT \log (a_{HCl_{II}}/a_{HCl_I}) + \text{constant}$.

Comparison of (5) with the equation $v = kc_{\cdot NCl}$ used in evaluating a velocity coefficient at any one acid concentration indicates that $k/a_{HCl}f_{\cdot NCl}$ should be constant at constant temperature, unless the speed is affected by viscosity.

Effect of Viscosity.—Since activities, and therefore activity equilibrium constants, are independent of viscosity, it is possible to show theoretically by consideration of the equilibrium, $A \rightleftharpoons P + Q$, that if the velocity of a unimolecular reaction is unaffected by viscosity, then that of a bimolecular reaction should also be unaffected; for application of the reaction-velocity equation to such an equilibrium gives $K = k_1/k_2$, and if K and k_1 are independent of viscosity, then k_2 must also be independent of it. This argument applies to any reaction-velocity equation of type (1).

In Table I the relative viscosities of the acid media (Green, J., 1908, **93**, 2023) have been included. The molalities (g.-mols. of acid per 1000 g. of water) are given in the first column, k' is the rate of chlorine formation, k'' the rate of hydrolysis of the chloroamine, $k = k' - k''$ is the rate of interaction of the chloroamine and hydrochloric acid, and a_{HCl} the activity measured electrometrically by Scatchard (*J. Amer. Chem. Soc.*, 1925, **47**, 641).

TABLE I.

C_{HCl}.	$10^3 . k'$.	$10^4 . k''$.	$10^3 . k$.	$a_{H\cdot}a_{Cl'}$.	$f_{\cdot NCl}$.	$\frac{k}{a_{HCl}f_{\cdot NCl}}$.	η.
0·1	0·52	0·32	0·49	0·00642	0·989	0·0767	1·000
0·2	1·88	0·58	1·82	0·02397	0·980	0·0775	1·005
0·3	4·06	0·96	3·95	0·05239	0·972	0·0775	1·011
0·4	7·11	1·25	6·98	0·09242	0·964	0·0783	1·017
0·5	10·8	1·50	10·6	0·1448	0·957	0·0772	1·023
0·6	16·0	1·92	15·8	0·2134	0·951	0·0778	1·029
0·7	21·9	2·24	21·7	0·2966	0·947	0·0779	1·035
0·8	29·1	2·54	28·9	0·3985	0·939	0·0773	1·042
0·9	38·2	2·88	37·9	0·5204	0·932	0·0779	1·043
1·0	48·2	3·24	47·9	0·6675	0·925	0·0776	1·054
1·5	124	4·80	124	1·843	0·877	0·0767	1·083

The values of $k/a_{HCl}f_{\cdot NCl}$ are constant to within 1%, which is of the order of the experimental error, whilst the viscosity changes by 8%. The observed rates of reaction may therefore be regarded as supporting the simple activity velocity equation for a reaction

between neutral molecules in aqueous media. They do not necessarily indicate that the reactivity of an ion is proportional to its thermodynamic activity.

On Brönsted's theory (*Z. physikal. Chem.*, 1922, **102**, 169),

$$v = kc_{:NCl}\, c_{HCl} f_{:NCl} f_{HCl} / f_{(:NCl,HCl)}$$
$$= kc_{:NCl}\, a_{HCl} f_{:NCl} / f_{(:NCl,HCl)},$$

and comparison with the simple activity equation shows that, in order to account for the observed facts, the activity coefficient of the critical complex (:NCl, HCl) must be constant to within 0·5% over the acid range examined (0·1—1·5*M*). This is unlikely in view of the solubility changes which apparently almost invariably occur on addition of electrolytes to a solution.

Experimental.

Measurement of the Solubility of N-*Chloroacetanilide in Acid and Salt Solutions.*—Excess of *N*-chloroacetanilide was added to the salt solution and shaken for 15 minutes at 25·0°; 10 c.c. of the clear solution were then removed by a pipette attached to a glass tube, on the lower end of which was mounted a perforated platinum plate covered with filter-paper. The chloroamine present was estimated by running it into acidified potassium iodide solution and titrating the liberated iodine with *N*/100-thiosulphate. The mean of four titrations was taken after saturation was attained (approx. 15 mins.). The measured solubilities of *N*-chloroacetanilide (in g.-mols. per litre) in potassium chloride, potassium nitrate, and nitric acid solutions are given in Table II, together with the calculated solubility in hydrochloric acid.

Table II.

Ionic strength.	0·0.	0·1.	0·4.	0·7.	1·0.	1·5.
Solubility in KCl ...	(0·01383)	0·01323	0·01232	0·01105	0·00963	0·00880
,, KNO_3 ·		0·01350	0·01325	0·01275	0·01243	0·01178
,, HNO_3 ·		0·01418	0·01511	0·01680	0·01935	0·02295
,, HCl ...		0·01398	0·01434	0·01461	0·01495	0·01577

Speed of Chlorine Formation from N-*Chloroacetanilide and Hydrochloric Acid.*—The effect of increasing the concentration of acetanilide, phenol, or *p*-cresol on the rate of fall of the iodine titre of a mixture of *N*-chloroacetanilide and hydrochloric acid is shown in Table III:

Table III.

HCl = 0·2*M* :NCl = 0·01*M*; temp. = 25·0°.

Concentration of phenol, *p*-cresol, or acetanilide, *M*	0·01.	0·02.	0·03.
100*k'* (acetanilide)	0·183	0·188	0·188
100*k'* (phenol)	0·186	0·188	0·188
100*k'* (*p*-cresol)	—	0·188	0·188

The limiting value for k which corresponds to the rate of chlorine formation from 0·01 M-chloroamine and 0·2M-hydrochloric acid is thus 0·00188. The limiting values for other acid concentrations are given in Table I. Care was taken when mixing the aqueous solution of chloroamine with the calculated weight of hydrochloric acid solution to adjust the initial temperatures so as to compensate for the heat of mixing. The speed of the reaction in the presence of 1·5M-hydrochloric acid is too great to allow of pipetting out portions of the mixture, and portions were therefore poured into weighed flasks containing potassium iodide and sodium acetate at 10-sec. intervals, the flasks were reweighed, and the contents titrated.

Speed of Hydrolysis of N-*Chloroacetanilide.*—Determinations of the rate of hydrolysis of the chloroamine were carried out in aqueous sulphuric, nitric, and perchloric acids, *p*-cresol being present in solution to remove the hypochlorous acid as formed. In the absence of acid, there is no detectable disappearance of the chloroamine in 7 hours. The rate of disappearance of chloroamine in the presence of acid follows a unimolecular velocity equation and the results obtained are summarised in Table IV.

TABLE IV.

:NCl = 0·01M; *p*-cresol = 0·1M; temp. = 25·0°.

Concentration of acid.	H_2SO_4.					HNO_3.	$HClO_4$.
	0·1	0·2	0·4	0·8	1·0	1·0	1·0
$k'' \times 10^4$	0·321	0·584	1·25	2·54	3·24	3·24	3·70

Summary.

1. Since concentration equilibrium constants are affected by the presence of electrolytes, the classical velocity coefficients are not true constants, and the use of an equation, $v = kf_{\text{catalyst}}C_AC_B$, for determining the effective concentration of the catalyst is not justifiable. Attention has therefore been redirected to the general form of a reaction-velocity equation.

2. The simplest type of the generalised equation applying to reactions involving neutral molecules, *viz.*, $v = ka_Aa_B$, is found to be in agreement with observations on the rate of interaction of hydrochloric acid and *N*-chloroacetanilide. The activities of the reagents used in the velocity equation are those which obtain in the presence of each other. Actually, the activity of the chloroamine was found to be progressively decreased by 13% as the hydrochloric acid concentration was increased from 0·1 to 1·5M.

3. The measurement of reaction speed in mols. transformed in unit time *per unit volume*, rather than per unit weight of solution, is justified on theoretical grounds.

4. A proof is advanced that reaction velocity is independent of viscosity.

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CCCLXIX.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part II. The Nitration of* 1-*Benzylpiperidine and of Some Related Substances.*

By ALFRED POLLARD and ROBERT ROBINSON.

ALTHOUGH it is now generally agreed that the *m*-directive effect of the ammonium-salt group in the benzylammonium salts is associated with the positive charge of the ion, there are still many aspects of the subject that call for elucidation. The majority of the constitutive influences that have been observed in this field are susceptible of simple explanations, for example, the somewhat higher *m*-direction in $CH_2Ph{\cdot}NMe_2$ than in $CH_2Ph{\cdot}NEt_2$ (Goss, Ingold, and Wilson, J., 1926, 2440) is the result to be anticipated from the theory of Allan, Oxford, Robinson, and Smith (J., 1926, 401), the terminal methyl groups in the latter compound having a smaller electron affinity than the hydrogen atoms which they may be regarded as displacing. Thus in the benzyldiethylammonium ion the positive charge of the nitrogen atom is neutralised by electron displacement towards it to a larger extent than is the charge of the nitrogen atom in the benzyldimethylammonium ion. Considerations like these, although frequently applicable, cannot be extended, however, to benzylpiperidine, from which the yield of *m*-nitro-derivative is notably higher than that from the closely related tertiary bases already mentioned. Noelting and Kregczy (*Bull. Soc. chim.*, 1916, **19**, 355) found that benzyldiethylamine on nitration in sulphuric acid solution gave from 35—40% of the *m*-nitro-derivative; Flürscheim and Holmes (J., 1926, 1562) found 33—53% under various conditions in sulphuric acid solution. Goss, Ingold, and Wilson (*loc. cit.*), employing nitric acid (*d* 1·5) alone, found that the proportion of the *m*-isomeride formed was 51%, and we have confirmed this. On the other hand, we were aware that the estimate of the proportion of the *m*-nitro-isomeride formed in

the nitration of benzylpiperidine, that was based by Ing and Robinson (J., 1926, 1665) on the separation as hydriodide, namely 60%, was a conservative one. Employing Francis and Hill's bromination method (*J. Amer. Chem. Soc.*, 1924, **46**, 2498), we find that 72% of *m*-nitrobenzylpiperidine is actually formed. Similarly, 1-β-*phenylethylpiperidine*, $C_5H_{10}N{\cdot}CH_2{\cdot}CH_2Ph$, obtained by the interaction of magnesium benzyl chloride and *N-iso*butoxymethylpiperidine in accordance with the general method of Robinson and Robinson (J., 1923, **123**, 532), gave on nitration about 22% of its *m*-nitro-derivative. This figure is higher than that found for the simpler dialkylated β-phenylethylamines (compare Goss, Hanhart, and Ingold, J., 1926, 250) and confirms the benzylpiperidine case. We are aware that this pronounced effect of ring closure may be accounted for merely as the result of a composition difference of two hydrogen atoms, our knowledge being insufficient to enable us to exclude this possibility on *a priori* grounds; we are nevertheless of the opinion that such a simple view is inadequate and, in the sequel, propose an alternative.

Flürscheim and Holmes (*loc. cit.*) showed that the proportion of *m*-nitrobenzyldiethylamine formed in the nitration of the salt of the base in sulphuric acid was diminished by saturation of the solution with ammonium sulphate. We have extended the study of this phenomenon to the nitration of benzylpiperidine in nitric acid solution. The addition of ammonium nitrate reduced the proportion of *m*-isomeride formed to about 56%; but as this salt is not readily soluble in nitric acid we made a further series of experiments on the influence of the addition of trimethylammonium nitrate to the acid, and found that the proportion of *m*-isomeride formed could be reduced to 16%. Addition of rubidium nitrate, which is readily soluble in nitric acid, produced roughly the anticipated effect. Addition of urea also decreased the proportion of the *m*-isomeride formed, and this was due to Flürscheim's effect and not to the removal of nitrous acid, because when nitric acid freed from nitrous acid by means of lead peroxide or by hydrogen peroxide was employed for the nitration of benzylpiperidine the normal proportion of the *m*-isomeride was formed.

These variations in orientation produced by the addition of salts are unexpectedly great and demonstrate that the condition of the kation is of primary importance in determining the nature of the observed results. We attribute the effect to the progressive electrostriction of the kations by the nitrate ions, an explanation which is the equivalent, in the modern theory, of Flürscheim and Holmes's suggestion that the ion undergoes substitution in the *m*-position and the undissociated salt in the *o*- and *p*-positions. On any theory, the

results make it evident that the value obtained in an experiment in which the base is gradually added to the nitric acid represents a mere average, since the ionic concentration is progressively increased during the nitration. This must coincide with a decreasing rate of formation of the *m*-isomeride relative to that of the *p*-isomeride. (Attempts to define and apply standard conditions are being made.) Nevertheless we have found that the results obtained in the nitrations are reproducible and, although the numbers representing the proportions of *m*-isomeride formed have not the character of fundamental constants, some conclusions may be drawn from a consideration of these averages obtained in the case of related bases. It would, for example, appear most probable that the proportion of *m*-isomeride formed is partly related to the existence of constitutive factors that either hinder or assist the operation of electrostriction of the kations. In this connexion stereochemical conceptions are of primary importance (compare Flürscheim's steric factor, *s*, in the correlation of the strengths of bases with their constitutions), because it is clear that the anions or negative ends of polarised complexes can the more effectively modify the field of the positively charged nitrogen atom the closer they can approach it. Other things being equal, we should expect the degree of electrostriction of the kations to be influenced as follows :

(1) *The smaller the number of atoms directly attached to the central charged atom, the greater should be the degree of electrostriction.* The present authors have studied the nitration of a benzyldiethylsulphonium salt and will shortly submit an account of the work. The proportion of *m*-isomeride formed, although still noteworthy, is very much lower than in the nitration of benzyltrimethylammonium nitrate. We attribute the result partly to the fact that the central atom is surrounded by four atoms in the ammonium salt, but by only three in the sulphonium salt. Benzylmethylpiperidinium nitrate, $CH_2Ph{\cdot}NMe{:}[CH_2]_5{}NO_3$, gave more than 90% of the *m*-nitro-derivative on nitration, and the proportion of the *m*-nitro-isomeride formed in the nitration of benzylpyridinium perchlorate was estimated to be about 67%. The nitrogen atom is attached to four atoms in the first case, but to only three in the second. This explanation of the result is adequate, but we do not exclude the possibility that the charge may be distributed over the pyridine nucleus to some extent by induction and may thus be less effective on account of electron displacements towards it.

(2) *The greater the volume of the central charged atom the greater should be the degree of electrostriction.* In this case, the larger radius might be expected to hinder electrostriction, but this effect may be

ignored, since it also places the charge further away from the aromatic nucleus, and this in itself diminishes the intensity of the field. On the other hand, electrostriction should be facilitated in the larger atoms by the smaller electron density near the surface rendering such atoms *softer* and perhaps by the appearance of patches not covered by the surrounding atoms. Thus under comparable conditions we may anticipate diminishing *m*-substitution in ascending a group in the periodic system: *e.g.*, $CH_2Ph{\cdot}NR_3 > CH_2Ph{\cdot}PR_3 > CH_2Ph{\cdot}AsR_3 > CH_2Ph{\cdot}BiR_3$, and $CH_2Ph{\cdot}SR_2 > CH_2Ph{\cdot}SeR_2$.

(3) *The smaller the space occupied by the atoms or groups attached to the central charged atom, the greater should be the degree of electrostriction.* This consideration clearly applies to the case of hydrogen atoms, which have even been regarded as embedded in the electron shells (Thomson, Paneth). The nakedness of the proton is necessarily a most important factor favouring electrostriction in the salts of primary, secondary, and tertiary bases in diminishing degree. In other examples, the electron displacements and distances separating the atomic centres must also be taken into account.

(4) *The greater the mobility of the groups surrounding the central charged atom, the greater should be the degree of electrostriction.* We imagine that closer approach of the anions is possible when the surrounding groups can be pushed aside or when, as the result of their normal vibrations, there are phases in which the nucleus of the central atom is exposed. Herein, we suggest, lies the explanation of the benzylpiperidine case. In benzyldiethylamine, the ethyl groups are not fixed, but may be supposed to be capable of some movement over a limited area of the surface of a sphere. When the ends of the chains are joined together as in benzylpiperidine, this freedom of movement must be lessened and electrostriction would be hindered in consequence. It is proposed to test this hypothesis by instituting further comparisons between open-chain and cyclic bases. The highest proportion of the *m*-derivative should be formed in the nitration of *N*-alpharylquinuclidinium salts, since the molecular framework in this series should be especially rigid.

The course of the nitration of benzylpiperidine was unaffected by the addition of nitromethane or ethyl malonate to the reaction mixture, and the addition of nitrobenzene only lowered the proportion of *m*-isomeride formed to 58%. Evidently these weak bases do not form true ionised salts with nitric acid, and we suggest the following conception of the nature of the solutions. It is generally recognised that, in an acid HX, X has a more or less pronounced affinity for the negative charge and by electron displacement the nucleus of the proton is bared so that HX is polarised. In a base

Be (e = electron) of the type that might form a salt BeH}X, B has a more or less pronounced affinity for the positive charge, and this molecule also is polarised (or there may be a tendency to polarisation consummated by induction). In an acid, therefore, there are an intense local positive field and a diffuse negative field; in a base, the negative field is the more concentrated. The respective complexes thus contain *bound* ions (although the charges are not integral), and the ever-changing interplay of the forces between these is the interpretation we offer of the expression " loose additive complex " which might be applied to the cases considered. This hypothesis gives a very similar picture of the condition of salts and of additive complexes in solution. In both cases, moderately stable molecules containing a limited number of the components may exist for definite periods of time.

EXPERIMENTAL.

Method of Estimation of the Proportion of m-*Isomeride formed.*—In applying the method of Francis and Hill (*loc. cit.*) to the products of nitration of benzylpiperidine, we found that the presence of small quantities of unchanged benzylpiperidine did not affect the results and that the best procedure was to analyse directly the mixture of bases obtained. An important precaution was the avoidance of too large an excess of titanous chloride or of bromine. The nitro-compounds present were first estimated by reduction with titanous chloride and back-titration with ferric alum; reduction with a slight excess of titanous chloride was then effected in a fresh experiment, followed by bromination at 0° with the usual precautions. Within the limits of experimental error, the pure *o*-, *m*-, and *p*-nitrobenzyl-piperidines (Lellmann and Pekrun, *Annalen*, 1890, **259**, 40) (purity estimated by means of titanous chloride, 99—100%) required after reduction 2, 3, and 2 molecular proportions of bromine, respectively. The fact that stoicheiometric rather than empirical relations can be employed in the calculations was confirmed by the analysis of the following mixtures: *ortho*, 48·4% and *meta*, 51·6% (Found: *meta*, 48, 51·4%); *meta*, 48% and *para*, 52% (Found: *meta*, 44, 47, 52%); *meta*, 71% and *para*, 29% (Found: *meta*, 69, 72%).

Nitration of Benzylpiperidine.—The nitration (of 5 g.) was carried out as described by Ing and Robinson (J., 1926, 1664) and the bases were isolated by means of ether. The mononitration was almost theoretical (Found: *meta*, 66, 71, 72, 76, 77; mean, 72%). In subsequent experiments, the conditions of nitration were the same (3 g. of the base and 20 c.c. of nitric acid, d 1·50) and the yields were from 90—98%. When relatively large amounts of ammonium nitrate were added, stirring was rendered difficult by the separation

of solids from the solution when it was cooled to −15°. These may contain $NH_4NO_3,2HNO_3$, but also, in all probability, a similar complex derived from benzylpiperidinium nitrate, because the proportion of the base that was nitrated under the standard conditions was very much lower than in other cases. The results were : addition of ammonium nitrate (5 g.) (Found : nitration, 95%; *meta*, 57, 59, 59%); addition of ammonium nitrate (7 g.) (Found : nitration, 17·8%; *meta*, 54, 58%); addition of ammonium nitrate (8 g.) (Found : nitration, 24·5%; *meta*, 54, 56%).

Lithium, sodium, potassium, and rubidium nitrates form a series in which the solubility in nitric acid increases, lithium nitrate being very sparingly soluble and rubidium nitrate being freely soluble. Addition of rubidium nitrate (3 g.) gave a clear reaction mixture (Found : nitration, 98%; *meta*, 19, 23·4, 25%). From the results tabulated below, it was found that the equivalent amount of trimethylammonium nitrate should reduce the proportion of the *m*-isomeride formed to 24%.

Trimethylammonium nitrate was crystallised from alcohol until its m. p. was 152—153°. The effects of additions of this salt are shown in the following table :

$NHMe_3NO_3$ added (g.).	Nitration (%).	*Meta* (%).	Mean.
0·5	98·3	59, 62, 66, 71	64
1·0	99·3	50, 53	51·5
1·5	96·0	40, 40, 41	40
2·0	98·7	30, 31, 33	31·3
3·5	81·3	15, 16, 17	16
7·0	90·9	21, 21	21

The result with 7·0 g., indicating a rise in *m*-isomeride formation after a minimum value has been reached, will be further investigated when the conditions are more accurately defined. The percentage nitration of the base in this case was confirmed by reducing the product (1·62 g.) with zinc and dilute sulphuric acid, the resulting amines being then benzoylated and the unchanged benzylpiperidine isolated by distillation in steam. The picrate (0·18 g.) was obtained in canary-yellow crystals, m. p. 174—176°; mixed with the picrate of benzylpiperidine, m. p. 175—177°, it melted at 174°. We were thus able to isolate as picrate 67% of the unchanged benzylpiperidine which the titanous chloride estimation indicated to have been present in the nitration product.

Since the rate of predominating *m*-substitution in a mono-substituted benzene derivative is always lower than that of predominating *op*-substitution (Holleman), it seemed possible that the degradation of the reagent might result in a diminution of the proportion of the *m*-isomeride formed. The gradient of the curve representing the relation between reaction velocity and chemical

activity of the reagent should, in other words, be steeper in the case of the formation of the *m*-isomeride. This consideration might have a bearing on the effect of addition of salts to the nitric acid, and we therefore tried another method of degradation, namely, the removal of nitrous acid. Urea (1·0 g.) was added to nitric acid (20 c.c.; *dl* ·51), which was then cooled in a freezing mixture and thereafter allowed to warm to the ordinary temperature (the density became 1·52); after cooling again, the mixture was employed in a nitration under the standard conditions (Found: nitration, 99%; *meta*, 45, 45%). Lead peroxide was added to nitric acid (*d* 1·53), mixed with a little acid (*d* 1·54) prepared by distillation of a mixture of nitric acid (*d* 1·51) and phosphoric anhydride; after filtration the acid had *d* 1·51 and was free from lead. The nitration was carried out with this specimen in the presence of a small amount of lead peroxide (Found: nitration, 94%; *meta*, 65, 69, 73%). Another specimen of nitric acid (*d* 1·5) was prepared by the addition of concentrated aqueous hydrogen peroxide to nitric acid (*d* 1·54), and this was employed in the nitration (Found: nitration, 98%; *meta*, 71%).

When the standard nitration conditions were modified by reduction of the volume of nitric acid to 10 c.c., a small diminution in the proportion of *m*-isomeride formed was observed (Found: nitration, 95%; *meta*, 61, 62, 64%), but when the volume of nitric acid employed for the nitration of 3 g. of the base was trebled (60 c.c.) some dinitration occurred.

The following results were obtained under the standard conditions modified as stated: Addition of nitrobenzene (5 g.) (Found: nitration, 98%; *meta*, 57, 59%); addition of nitromethane (2·5 g.) (Found: nitration, 99%; *meta*, 70, 73, 73%); addition of ethyl malonate (6·5 g.) (Found: nitration, 97%; *meta*, 69, 69%).

Benzyldiethylamine was nitrated under the conditions used for benzylpiperidine (Found: nitration, 98%; *meta*, 48, 50, 51%).

Nitration of Benzylmethylpiperidinium Nitrate.—Benzylmethylpiperidinium iodide, prepared from benzylpiperidine and methyl iodide, crystallises from ethyl alcohol in colourless needles, m. p. 147° (Found: I, 40·0. $C_{13}H_{20}NI$ requires I, 40·1%). It is readily soluble in water and in hot alcohol.

This salt was converted into the *nitrate* by exact decomposition with silver nitrate, and the aqueous solution was evaporated to a syrup and then in a vacuum over sulphuric acid for several months. The friable solid was extremely hygroscopic, liquefying in the air in a few seconds; an estimation by means of nitron, combined with a titration showing the amount of free nitric acid present, indicated that the material contained 99—100% of the quaternary nitrate.

The salt (20 g.) was added to nitric acid (80 c.c.; *d* 1·5) at 0° during 15 minutes, and the solution kept at this temperature for 2 hours and at room temperature for 2 hours more. The liquid was then diluted and distilled under diminished pressure, and this process was repeated so as to remove most of the nitric acid. The residue was neutralised with ammonia, and the picrate precipitated by stirring for 1 hour with an excess of picric acid. The mixture of picrate and picric acid was collected, washed with aqueous picric acid, and mechanically shaken with ether and dilute hydrochloric acid until no solid remained. The acid aqueous solution was concentrated under diminished pressure, again extracted with ether, and then neutralised with ammonia and concentrated to about 100 c.c. The iodide was then precipitated by the addition of a large excess of sodium iodide (yield, 94%). The crude nitration product (10 g.) was fractionally crystallised from methyl alcohol; 9·7 g. of the pure *m*-isomeride were obtained (Found: I, 35·0%), and the colour reactions of the last mother-liquor showed that it still contained the *m*-isomeride in preponderating amount, a little of the *p*-isomeride, and a yellow impurity.

The three nitrobenzylmethylpiperidinium iodides were prepared from the nitrobenzylpiperidines and methyl iodide and dried at 100° for analysis. o-*Nitrobenzylmethylpiperidinium iodide* crystallises from methyl alcohol in intensely yellow prisms, m. p. 183—184° (Found: I, 34·9. $C_{13}H_{19}O_2N_2I$ requires I, 35·1%). This salt develops a brownish-yellow colour in boiling methyl-alcoholic potassium hydroxide, and on the addition of a methyl-alcoholic solution to acetone and solid potassium hydroxide a bright brownish-red solution is obtained.

m-*Nitrobenzylmethylpiperidinium iodide* crystallises from methyl or ethyl alcohol in very pale yellow needles which darken at 198° and melt at 204° (Found: I, 35·1%). It gives no coloration in boiling methyl-alcoholic potassium hydroxide, but when a methyl-alcoholic solution is added to acetone and solid potassium hydroxide an intense and characteristic violet colour is developed.

p-*Nitrobenzylmethylpiperidinium iodide* crystallises from water or methyl alcohol in large, well-developed, yellow prisms, and from ethyl alcohol in pale yellow needles, m. p. 188° (decomp.) (Found: I, 34·9%). This salt develops a reddish-brown coloration in boiling methyl-alcoholic potassium hydroxide, and a dull mauve-red one when a methyl-alcoholic solution is added to acetone and solid potassium hydroxide.

These salts exhibit colour reactions under other conditions, but those recorded above were selected, after numerous trials, for the purpose of assisting in the identification of specimens. It will be

observed that under one set of conditions the *m*-isomeride gives no reaction whereas the *o*- and *p*-isomerides develop colorations; under the other set of conditions the *m*-isomeride gives the most characteristic reaction.

Nitration of Benzylpyridinium Perchlorate.—Aqueous perchloric acid was added to a solution of benzylpyridinium chloride; the precipitated oil crystallised in contact with ice-water. The dry salt (20 g.) was added during 45 minutes to nitric acid (100 c.c.; *d* 1·5) at 0°; the mixture was kept at this temperature for 1 hour and then allowed to warm to the temperature of the room during 1·5 hours. The solution was diluted, the greater part of the nitric acid distilled under diminished pressure, an excess of perchloric acid (*d* 1·12) added, and the mixture kept in the ice-chest for 24 hours; the precipitated perchlorates were then collected, washed, and dried (A) (20·5 g.) (Found: C, 45·8; H, 3·6. $C_{12}H_{11}O_6N_2Cl$ requires C, 45·9; H, 3·5%). In another experiment, the nitric acid was not removed and the crystallisation of the perchlorates was carried out fractionally, crops of approximately 12 g., 5 g., and 3 g. being obtained. On recrystallisation, the first fraction gave pure *m*-nitrobenzylpyridinium perchlorate, but the separation could not be carried out in a quantitative manner. Oxidation of the crude nitration product with potassium permanganate gave *m*- and *p*-nitrobenzoic acids, which were separated and identified; the yields, however, were not satisfactory. It was found possible to apply Francis and Hill's bromination method to this case, because the nitrobenzylpyridinium perchlorates may be quantitatively reduced to aminobenzylpyridinium chlorides by means of titanous chloride. This is not effected, however, under the ordinary conditions and the following experiment indicates the modifications required. A solution of *p*-nitrobenzylpyridinium perchlorate (0·1000 g.) in 50% sulphuric acid (25 c.c.) and water (150 c.c.) was boiled with titanous chloride for 20 minutes with the usual precautions, care being taken to avoid undue concentration (Found: titanous chloride solution used, 37·2 c.c. Calc. for complete reduction, 37·3 c.c.). Applying this method of reduction to the product (A), followed by bromination in the usual manner, we found *meta*, 64, 69, 69%. A mixture of *m*-nitrobenzylpyridinium perchlorate (70%) and *p*-nitrobenzylpyridinium perchlorate (30%) was similarly analysed (Found: *meta*, 69, 71%).

The isomeric nitrobenzylpyridinium perchlorates were prepared by addition of perchloric acid to solutions of the corresponding chlorides or bromides.

o-Nitrobenzylpyridinium perchlorate crystallises from alcohol in colourless, elongated, rhombic prisms, m. p. 155—156° (Found: C,

46·1; H, 3·5. $C_{12}H_{11}O_6N_2Cl$ requires C, 45·9; H, 3·5%). The action of boiling aqueous sodium hydroxide on this salt causes a decomposition, one of the products of which is *o*-nitrotoluene.

m-*Nitrobenzylpyridinium perchlorate* crystallises from alcohol in colourless, prismatic needles, m. p. 176—177° (Found: C, 46·0; H, 3·6%).

p-*Nitrobenzylpyridinium perchlorate* crystallises from alcohol in colourless, elongated laminæ, m. p. 181—182° (Found: C, 46·0; H, 3·6%). The long, flat plates have jagged edges and well-formed pointed or square-cut ends and exhibit a strong twinning tendency. On boiling with sodium hydroxide solution, *p*-nitrotoluene is produced.

1-β-*Phenylethylpiperidine.*—The preparation of 1-*iso*butoxymethylpiperidine (McLeod and G. M. Robinson, J., 1921, **119**, 1474) is conveniently carried out on a moderately large scale. A mixture of piperidine (400 g.) and *iso*butyl alcohol (400 g.) was added to 40% aqueous formaldehyde solution (400 g.) with cooling in running water; the mixture was saturated with potassium carbonate and kept over-night and the oil was then dried with fresh potassium carbonate. On distillation, 665 g., b. p. 200—210°, were obtained (yield, 83%). The considerations dictating the use of *iso*butyl alcohol are that the higher alcohols give the better yields, and that some decomposition occurs in the distillation of 1-*n*-butoxymethylpiperidine under ordinary pressure. *iso*Butoxymethylpiperidine (120 g.) was slowly added to an ethereal solution of magnesium benzyl chloride (from 100 g. of benzyl chloride, 20 g. of magnesium, and about 1500 c.c. of ether), a violent reaction ensuing after each addition. Water was then cautiously introduced with shaking until a clear ethereal layer could be decanted from the magnesia sludge; the latter was washed with fresh ether. The base was extracted from the ethereal solution by successive small volumes of dilute hydrochloric acid, and any unchanged *iso*butoxymethylpiperidine decomposed by heating the acid solutions for 15 minutes on the steam-bath. The base was then set free by means of sodium hydroxide, separated, dried with sodium hydroxide, and distilled. 105 G., b. p. 162°/35 mm., of a colourless oil were obtained (yield, 80% calculated on the *iso*butoxymethylpiperidine) (Found: equiv., 189·3. Calc., 189·2). The b. p. /760 mm. was 262—264° with some decomposition. The *picrate* crystallised from alcohol in perfectly straight, canary-yellow needles, m. p. 144—145° (Found: N, 13·4. $C_{19}H_{22}O_6N_4$ requires N, 13·4%). The length of the individual crystals seems to be limited only by the shape of the container and the volume of the solution; those which we obtained were about 8—10 cm. long.

On nitrating the base under the conditions used for benzylpiperidine, and assuming the stoicheiometric relation for the bromination of the *m*- and *p*-amino-derivatives, we found: nitration, 98%; *meta*, 20, 22·7, 24%.

1-γ-*Phenylpropylpiperidine*, $CH_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}[CH_2]_5$.—The method described in the last section was applied, the initial materials being phenylethyl bromide (98 g.), magnesium (12·5 g.), and *iso*butoxymethylpiperidine (85 g.). 59 G. of a colourless oil, b. p. 150°/15 mm., were obtained (yield, 58%) (Found: equiv., 202. Calc., 203). This base has b. p. 272—274°/760 mm. with decomposition. The *picrate* crystallises from alcohol in bright yellow tablets, m. p. 99—100° with slight previous softening (Found: N, 13·0. $C_{20}H_{24}O_6N_4$ requires N, 13·0%).

In this case, nitration with nitric acid (*d* 1·5) causing some dinitration, the standard conditions were employed with nitric acid having *d* 1·465 (Found: nitration, 99%; *meta*, 5, 6, 8%).

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CCCLXX.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part III. The Nitration of* m-*Nitrophenylbenzylsulphone.*

By BIBHUCHARAN CHATTERJEE and ROBERT ROBINSON.

THE hypothesis (Allan, Oxford, Robinson, and Smith, J., 1926, 401) that the positive charge of the dipole in the nitro-group of phenylnitromethane is the cause of the *m*-substitution observed by Holleman, and the related wider theory, can be tested experimentally in many directions, the most obvious of which is the study of the orienting influence in aromatic substitution of polar and dipolar groups situated at various distances from the nucleus. This field of systematic work is too large to be covered by any one group of investigators, but the exploitation of it by Ingold and his co-workers has involved some duplication of research, particularly in connexion with the nitration of phenylethylamine derivatives and of substances of the forms $Ph{\cdot}CO{\cdot}R$ and $Ph{\cdot}CH_2{\cdot}SO_2R$. Some preliminary experiments in the latter group are described in this and the following communication.

The interest of the toluene-ω-sulphonyl compounds resides in their theoretical analogy with the phenylnitromethanes, the double dipole $-\overset{+}{S}\overset{+}{O}_2$ being compared with the single dipole $-\overset{+}{N}O_2$, and in the fact that the effect of varying the group R can be observed. We selected the case of *m*-nitrophenylbenzylsulphone because we thought that the group $-C_6H_4\cdot NO_2(m\text{-})$ should be almost neutral and the results could therefore be ascribed to the influence of the sulphone group. The proportions of the *o*-, *m*-, and *p*-isomerides formed on nitration, estimated by colorimetric methods which are fully described in the experimental section, were approximately 25, 28, and 47%, respectively. The double semi-polar double bond of the sulphone group has thus a smaller *m*-orienting effect than the single semi-polar double bond of the nitro-group. This constitutes a definite argument against the view that the charges in the semi-polar double bonds are integral and effective as such.

As Born (compare *Ann. Reports*, 1926, 261) has shown, kations and anions are distorted and polarised in the neighbourhood of each other, and if this is true of the components of a molecule of sodium chloride, how much more must it be true of the bound ions in a semi-polar double bond. In fact, the intensity of the external fields may be chiefly governed by this atomic polarisation. On this basis, we may conclude that the kationic charge of the sulphur atom in the sulphone group is less effective than that of the nitrogen in the nitro-group and that this is due to the relatively greater degree of polarisation of the oxygen atoms in the sulphone; this again is clearly connected with the larger nuclear charge of the sulphur atom and the smaller electron density of its outer shell.

Ingold, Ingold, and Shaw (this vol., p. 813) found that the nitration of benzylmethylsulphone gave about 30% of the *m*-nitro-isomeride, but these authors attributed the result (comparison with phenylnitromethane) to absorption of the effect of the ionic charge of sulphur in passing through the outer shells of the atom. This suggestion appears to be fallacious owing to the circumstance that in the calculation of the kationic charges, for example, + 1, + 2, or + 6, in various theories respecting sulphur compounds, the electrons of the outer shells are taken into account or assumed to be donated to other atoms. Probably the distance separating the centres of sulphur and carbon atoms in C—S is greater than that separating the centres of carbon and nitrogen atoms in C—N and this must reduce the effectiveness of equivalent charges in accordance with Coulomb's Law; if the charges are not equivalent, the validity of this explanation is greatly impaired.

Our view that the bound oxygen ions are polarised, thus reducing

the net charge of the sulphur atom, is closely connected with the theory of electrostriction of sulphonium kations by free anions; it is, in fact, intramolecular electrostriction. It should be noted that this hypothesis emphasises the importance of the part played by the central atom and can be correlated experimentally with work on the distribution of electrons in crystals. The hypothesis is also connected with the strength of the sulphonic acids, for it is surely the polarisation of the oxygen atoms in the $R{\cdot}SO_3$ ion that loosens the grip of their electrons on the proton (alternatively, increases the repulsion of the proton by the oxygen nucleus).

EXPERIMENTAL.

m-*Nitrophenylbenzylsulphone*, $NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2Ph$.—A mixture of sodium *m*-nitrobenzenesulphinate (20 g.), benzyl chloride (15 g.), and 95% alcohol (60 c.c.) was refluxed for 4 hours, and the product (18 g.) precipitated by the addition of water. The *sulphone* crystallised from alcohol in very pale yellow needles, m. p. 151—152° (Found: C, 56·8; H, 4·5; N, 5·2. $C_{13}H_{11}O_4NS$ requires C, 56·3; H, 4·0; N, 5·1%).

m-*Nitrophenyl*-o-*nitrobenzylsulphone* was similarly prepared from *o*-nitrobenzyl chloride (8 g.), the yield being 14·7 g. It crystallised from acetone in pale yellow plates, m. p. 192—193° (Found: C, 48·6; H, 3·5; N, 9·0. $C_{13}H_{10}O_6N_2S$ requires C, 48·5; H, 3·1; N, 8·7%).

m-*Nitrophenyl*-m-*nitrobenzylsulphone* crystallised from alcohol in almost colourless, microscopic cubes, m. p. 194—195° (Found: C, 48·5; H, 3·0; N, 8·5%).

m-*Nitrophenyl*-p-*nitrobenzylsulphone* crystallised from acetone in very pale yellow needles, m. p. 180—181° (Found: C, 48·8; H, 3·6; N, 9·0%). The three isomerides are very sparingly soluble in most organic solvents and although the *o*-isomeride is the most sparingly soluble in alcohol, neither this nor any other solubility property could be employed for their separation.

Nitration of m-*Nitrophenylbenzylsulphone*.—The finely powdered substance (5·00 g.) was gradually added during 15 minutes to nitric acid (40 c.c.; *d* 1·5) kept at $-5°$ to 0°. Each addition produced a brownish-red, evanescent coloration. After 1 hour, the mixture was allowed to reach the room temperature and the product was precipitated by water after 3 hours. It was ground under water, washed, and dried (5·63 g. or 97%). In a second similar experiment the yield was 98·5% (Found: C, 48·6; H, 3·4%).

Various attempts to fractionally crystallise this material were made, but no suitable solvent could be found, and after experi-

menting with oxidation methods, which also we were compelled to abandon on account of the sparing solubility of the isomerides, we adopted the following colorimetric method. The *p*-isomeride gives a carmine coloration in alcoholic solution on the addition of 10% aqueous sodium hydroxide, whereas the *o*- and *m*-isomerides give no coloration under these conditions. In dilute solutions, the intensity of this colour was roughly proportional to the concentration of the *p*-isomeride and it was not affected by the presence of the *o*- or *m*-isomeride. A Zeiss "Stufenphotometer" was employed for the measurements and all the comparisons were direct, and not through a standard. The liquids were mixed in the adjustable vessels so that the colours could be compared as quickly as possible, and stirring was necessary before the caps were screwed on. Remarkably consistent results were obtained. Solutions of the nitration product (0·1987 g.), the *o*-isomeride (0·2018 g.), the *m*-isomeride (0·2098 g.), and the *p*-isomeride (0·2023 g.) in absolute alcohol (1000 c.c. each) were prepared. Taking 10 c.c. of the standard solution and adding 2 c.c. of 10% aqueous sodium hydroxide, it was found that the solution of the *p*-isomeride was roughly twice as concentrated (in *p*-isomeride) as the solution of the nitration product, columns of 5·35, 6·0, and 6·9 mm. balancing columns of 10·7, 11·9, and 13·8 mm., respectively. A closer comparison was then made by diluting the solution of the *p*-isomeride with an equal volume of alcohol and producing the colour as before; the solution of the *p*-isomeride was distinctly the stronger, the measurement indicating that the nitration product contained 47% of the *p*-isomeride. A mixture of the solution of the *p*-isomeride (45 c.c.) and alcohol (55 c.c.) gave a perceptibly weaker colour than the solution of the nitration product, the measurement again indicating that the nitration product contained 47% of the *p*-isomeride. The experiment was twice repeated with exactly the same results, so that the determination of the proportion of the *p*-isomeride in the mixture was considered to be sufficiently accurate to be employed in further work.

The estimation of the proportions of the *o*- and *m*-isomerides was much more difficult and the method was not capable of very great accuracy; the experiments were, however, frequently repeated and it is hoped that the results are not seriously in error. The *o*-isomeride gives an intense violet coloration with strong alkalis in alcoholic acetone (or pure acetone) solution, whereas the *m*-isomeride gives no immediate coloration. The following solutions were employed: (1) *o*-isomeride (5 c.c.), *p*-isomeride (20 c.c.), alcohol (17·5 c.c.); (2) *o*-isomeride (10 c.c.), *p*-isomeride (20 c.c.), alcohol (12·5 c.c.); (3) *o*-isomeride (15 c.c.), *p*-isomeride (20 c.c.), alcohol

(7·5 c.c.); (4) *o*-isomeride (20 c.c.), *p*-isomeride (20 c.c.), alcohol (2·5 c.c.); (5) nitration product (42·5 c.c.). Sodium ethoxide solution (10 c.c.) (from 10 g. of sodium in 250 c.c. of alcohol) and then pure acetone (50 c.c.) were added to each mixture. The colour developed by the nitration product was found to lie between those produced by solutions (2) and (3) and was much closer to that of (2). Experiments with solutions of compositions between those of (2) and (3) confirmed this and indicated that the nitration product contained 25—30% of the *o*-isomeride. The colour-tone match was not perfect, however, and it was then noticed that the *m*-isomeride slowly developed a brownish-red coloration in acetone solution in the presence of sodium ethoxide. A fresh series of solutions was therefore made up in which the pure alcohol was replaced by the appropriate volume of the *m*-isomeride solution; a colour-tone match was then obtained and the intensity showed that the proportion of the *o*-isomeride in the nitration product was 23—27%. This was confirmed by a direct estimation of the content of *m*-isomeride.

The three isomerides develop colorations when solid potassium hydroxide is added to their cold solutions in acetone, but if, after a short time, water is added, the colorations due to the *o*- and *p*-isomerides are discharged and the *m*-isomeride gives a brownish-yellow solution. A series of mixtures was prepared as before from the standard alcoholic solutions and, after the alcohol had been removed, acetone (30 c.c.) and potassium hydroxide (2 cm. stick) were added. The mixture was stirred for 5 minutes, water (50 c.c.) was then added, and the colour compared with that obtained from the nitration product under identical conditions. The proportion of the *m*-isomeride in the nitration product was thus found to lie between 25 and 32%. A mixture of the *o*-isomeride (0·250 g.), the *m*-isomeride (0·280 g.), and the *p*-isomeride (0·470 g.) was then made and its colour reactions were compared with those of the nitration product, the substances being weighed on a micro-balance, with the result that no difference could be detected. The mixture after fusion, resolidification, and grinding had m. p. 152—156° and the nitration product had m. p. 153—157°; a mixture of the two had m. p. 152—156°.

The authors wish to express their indebtedness to the Chemical Society for a grant which defrayed a part of the cost of the investigation.

THE UNIVERSITY, MANCHESTER. [*Received, September 9th*, 1927.]

CCCLXXI.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part IV. The Nitration of Toluene-ω-sulphonic Acid and of Toluene-ω-sulphonyl Chloride.*

By Arthur C. Bottomley and Robert Robinson.

The work of Vorländer (*Ber.*, 1919, **52**, 262) proved that an atom bearing a positive charge when directly attached to the aromatic nucleus has a powerful *m*-directive effect, and on the lines of electronic theories this may be interpreted as meaning that a group having a strong attraction for electrons has a *m*-directive effect. The discovery of the largely predominating *meta*-nitration of benzyltrimethylammonium nitrate (Part I, J., 1926, 1655) justified this view in the most convincing manner. It may be fairly claimed that the connexion between polarity and orientation thus firmly established is less hypothetical in character than any other in organic chemistry. The proof that *m*-substitution in benzene derivatives is *sometimes* due to a general electrical effect of the first substituent suggests that *m*-direction may *always* be initiated in this way.

Among *m*-directive groups the only one which seems to present difficulty from this point of view is the sulphonic acid group. At first sight it is hard to reconcile the net negative charge of the sulphonic ion with an assumed tendency to attract electrons. It must be remembered, however, that sulphuric acid is a powerful dibasic acid and therefore $HS\bar{O}_4$, which may be written $HO{\cdot}S\bar{O}_3$, is evidently able to donate a proton to acceptor molecules, and this means that the $-S\bar{O}_3$ group, in spite of its charge, retains a high electron affinity. The phenomenon is doubtless connected with incomplete neutralisation of the charge of the sulphur atom by the distorted oxygen ions surrounding it (see the preceding communication) and with the partial neutralisation of the field of the oxygen ions by neighbouring kations and kationoid complexes.

The possibility that the sulphonic acid group is *m*-directive for the same reason that the ammonium-salt group is *m*-directive would become a probability if it could be shown that the effect is produced when a saturated carbon atom separates the sulphur atom from the benzene nucleus; we accordingly studied the nitration of toluene-ω-sulphonic acid. This substance is nitrated to a predominating extent in the *op*-positions, but the proportion of the

m-nitro-isomeride produced is much greater than that obtained in the nitration of toluene. This result confirms the view that the sulphonic ion group, $\bar{S}O_3$, has a higher electron affinity than has a hydrogen atom, and we may confidently attribute the *m*-substitution of benzenesulphonic acid to the occurrence of the condition $Ph\longrightarrow\bar{S}O_3$.

Toluene-ω-sulphonyl chloride, $Ph\longrightarrow CH_2\overset{(a)}{\longrightarrow}SO_2\overset{(b)}{\longrightarrow}Cl$, may be regarded as a sulphone in which the normal displacement (a) is reinforced by that (b) due to the chlorine atom. In harmony with our theory, the percentage of the *m*-isomeride formed in the nitration of this substance is much greater than that formed in the nitration of toluene-ω-sulphonic acid and considerably greater than that formed in the nitration of benzyl-*m*-nitrophenylsulphone.

The publication of Ingold, Ingold, and Shaw (this vol., p. 813), dealing with the nitration of substances of the form $CH_2Ph{\cdot}SO_2R$, appeared when our work was at a stage where the determinations of the proportion of *m*-isomeride formed in the nitrations had been completed. In view of it, the experimental section of this communication has been curtailed so that all repetition of description has been avoided. We carried out, for example, identifications of the products as nitrotoluene-ω-sulphonamides (compare Mohr, *Annalen*, 1883, **221**, 218; Purgotti and Monti, *Gazzetta*, 1900, **30**, ii, 254) and no further reference to this part of our work is deemed necessary.

Experimental.

Method of Estimation of the Proportion of m-*Isomeride formed in the Nitrations.*—Francis and Hill's method of bromination after reduction of the nitro-compounds with titanous chloride (*J. Amer. Chem. Soc.*, 1924, **46**, 2498) has been found to be applicable to the sodium nitrotoluene-ω-sulphonates. Small corrections were applied for the deviations from the stoicheiometric relations found for sodium *o*-, *m*-, and *p*-nitrotoluene-ω-sulphonates.

Sodium *o*-nitrotoluene-ω-sulphonate was crystallised from semi-saturated brine and dried at 100—120° (Found: NaCl, 20·3; sodium nitrotoluenesulphonate estimated by titanous chloride, 79·4%). On reduction and bromination, the deviation from the theoretical value (in the volume of potassium bromate solution required for bromination) was − 0·4%. Sodium *m*-nitrotoluene-ω-sulphonate was crystallised from semi-saturated brine and dried at 130—140° (Found: NaCl, 7·1; sodium nitrotoluenesulphonate, 92·4%; deviation from theory on reduction and bromination, + 0·9%). The *o*-isomeride loses $1H_2O$ at 100°, but the *m*- and *p*-isomerides retain their water of crystallisation below 125°. Sodium

p-nitrotoluene-ω-sulphonate was crystallised from brine and dried at 140° (Found: NaCl, 1·9; sodium nitrotoluenesulphonate, 96·6%; deviation from theory on reduction and bromination, + 1·1%).

Some difficulty was experienced in obtaining satisfactory end-points in the final titrations with sodium thiosulphate, and this was overcome by using not too large an excess of bromine and by neutralising part of the acid after the liberation of iodine.

Nitration of Sodium Toluene-ω-sulphonate.—Sodium toluene-ω-sulphonate crystallised from 95% alcohol in lustrous leaflets, and the specimens employed were anhydrous and free from sodium chloride.

In a preliminary experiment, 20 g. of the salt were nitrated and 16·5 g. of washed sodium nitrotoluenesulphonates (dried at 100°) were obtained (Found: loss at 140° or H_2O, 6·0; NaCl, 8·6; sodium nitrotoluenesulphonates, 85·3%; *meta*, 20·2, 19·8, 18·5, 19·4%). The true yield was 57·6% and therefore the minimum value for the proportion of *m*-isomeride formed is 11—12%.

In attempts to improve the yield products were obtained containing sodium nitrate, which interfered seriously with the determinations. In subsequent experiments, the absence of nitrates was always confirmed.

Ultimately, the following nitration conditions were adopted: Sodium toluene-ω-sulphonate (10 g.) was added during 30 minutes to nitric acid (15 c.c.; *d* 1·5) at 0°, a further quantity of the acid (5 c.c.) being used to wash the sides of the container. Three hours from the commencement the ice-bath was removed and 1 hour later the solution was mixed with water (120 c.c.) and neutralised by means of sodium carbonate (20 g.), and after the addition of sodium chloride (30 g.) the liquid was heated until a clear solution resulted. The cooled liquid was kept at 0° for 3 hours and the separated solid was then washed twice with 15% brine (10 c.c.) and dried at 100° (Specimen A, 12·8 g.) (Found: H_2O, 4·9; NaCl, 10·0; sodium nitrotoluenesulphonate, 84·8%; *meta*, 11·7, 11·0, 10·6, 10·3, 9·6, 9·6%). The yield of sodium nitrotoluene-ω-sulphonates was therefore 88% and the minimum value for the proportion of *m*-isomeride formed is 9·2% (maximum, 21·2%). Another specimen (B) was prepared in the same manner (purity, 82%; true yield, 88%).

Nitration of Toluene-ω-sulphonic Acid.—The free acid (9 g.), prepared by Böhler's method (*Annalen*, 1870, **154**, 50), was treated exactly as described above for its sodium salt. The isolated, washed, and dried solids amounted to only 8·0 g. A further amount of sodium chloride (20 g.) was therefore added and 6·0 g. of the

mixed salts were obtained. The products were free from nitrates and were mixed (Found: H_2O, 3·3; NaCl, 39·9; sodium nitrotoluenesulphonates, 56·8%; *meta*, 14·2, 13·7, 14·2%). Here the true yield was 63·6% and the minimum value for the proportion of *m*-isomeride is 8·9%. We are unable to account for the variations in yield which were observed, but since the actual amount of the *m*-isomeride obtained was as great in this experiment (yield, 64%) as in the one previously described (yield, 88%), we may conclude that the proportion formed is greater in the nitration of the acid than in that of the salt. The point is not raised in the introduction, because it is hoped to follow up this indication by fresh experiments before the interesting theoretical implications are discussed.

Nitration of Toluene-ω-sulphonyl Chloride.—Toluene-ω-sulphonyl chloride (10 g.) was added during 30 minutes to nitric acid (15 c.c.; *d* 1·5) at 0°, a further amount of nitric acid (5 c.c.) being employed to wash the sides of the container. After 3 hours, the ice-bath was removed and 1 hour later the product was precipitated by water, collected, and boiled with a solution of sodium carbonate (11 g.) in water (100 c.c.) until no oil remained (about 1 hour). The liquid was filtered hot, sodium chloride (20 g.) introduced, and the mixture kept at 0° for 3 hours; the separated solid was then collected, washed twice with 15% brine (10 c.c.) at 0°, and dried at 100° (yield, 10·2 g.) (Found: H_2O, 5·7; NaCl, 12·3; sodium nitrotoluenesulphonates, 77·6%; *meta*, 44%). The yield was 63% and the minimum value for the proportion of *m*-isomeride formed is 28%. The specimen contained carbonate, and this probably accounts for the fact that the water, sodium chloride, and nitrocompounds determined totalled only 95·6%. Another nitration was carried out in exactly the same manner, but the alkaline solution was neutralised with hydrochloric acid and the sodium nitrotoluenesulphonates were salted out in two crops (mixed, 15·7 g.) (Specimen C) by means of sodium chloride (total, 50 g.) (Found: H_2O, 3·8; NaCl, 40·2; sodium nitrotoluenesulphonates, 55·8%; *meta*, 56, 54, 56, 56%). The true yield was 70·5% and the minimum value for the proportion of *m*-isomeride formed is 39% (maximum, 67·5%).

Comparison of these experiments shows that more efficient salting out increases the percentage of the *m*-isomeride in the product, and hence the true value for the *m*-isomeride content should be considerably greater than the minimum; it must also, of course, be much less than the maximum.

Estimation of the Proportions of the p-*Isomeride in Specimens A, B, and C.*—On heating at 100° with concentrated aqueous potassium hydroxide, the *o*- and *m*-nitrotoluene-ω-sulphonates

develop no coloration, whereas the *p*-isomeride gives a yellowish-orange solution. Attempts to apply this reaction in a colorimetric method gave unintelligible results until it was found that the colour produced by the *p*-isomeride is more intense in the presence of the *o*-isomeride and still more intense in the presence of the *m*-isomeride. The *o*- and *m*-isomerides give no coloration when mixed and heated with aqueous potassium hydroxide.

Solutions were made up to contain 1·0% of the pure *o*-, *m*-, and *p*-isomerides and of the nitro-compounds in specimens A, B, and C. 10 C.c. of one of these solutions or of a mixture of them were mixed with 25 c.c of a solution of potassium hydroxide (100 g.) in water (100 c.c.) and heated in a bath of boiling water for about 2 hours. All the comparisons were direct under identical conditions, and in addition to the determination of the intensity of the colour the rapidity of its appearance afforded valuable guidance. In making up the standards, the ascertained percentage of the *m*-isomeride in the specimen to be tested was introduced and kept constant, the proportions of the *p*- and *o*-isomerides being varied.

In the case of specimen C, the colour was practically identical with that of a standard made from 5·5 c.c. of the *m*-isomeride solution and 4·5 c.c. of the *p*-isomeride solution and was distinctly stronger than that obtained from the standard—*m*-, 5·5; *p*-, 4·0; *o*-, 0·5 c.c. The colours were estimated after dilution of the solutions to 40 c.c. by means of the Zeiss "Stufenphotometer." The specimen C, obtained in 70·5% yield from the nitration of toluene-ω-sulphonyl chloride, does not, therefore, contain an appreciable amount (<5%) of the *o*-isomeride.

No difference could be detected in the behaviour of the specimens A and B when a direct comparison was made; most of the experiments were therefore made with B, because a larger quantity of this specimen was available. A series of comparisons with standards showed that the colour derived from B was more intense than that from the standard—*m*-, 1·0; *p*-, 4·5; *o*-, 4·5 c.c., and less intense than that from the standard—*m*-, 1·0; *p*-, 5·0; *o*-4·0 c.c.

The actual intensity measurements of these and four other standards compared with the solution from B were used to construct a graph, by means of which the solution exactly equivalent to the B solution was found to be—*m*-, 1·0; *p*-, 4·8; *o*-, 4·2 c.c. This was experimentally confirmed with solutions made up from quantities weighed on a micro-balance.

A specimen was made by admixture of the *o*-, *m*-, and *p*-isomerides and sodium chloride that contained 82% of the pure sodium nitrotoluene-ω-sulphonates (*m*-, 10; *o*-, 40; *p*- 50%) and was found

in numerous quantitative trials under different conditions to resemble B closely in behaviour. The colours were developed a very little the more rapidly with the artificial mixture. Finally, the specimen A was reproduced on the same basis and with the same results.

The colour reactions observed with alkaline solutions also guarantee the absence of sodium dinitrotoluene-ω-sulphonates. A specimen of the latter (probably the 2 : 4-dinitro-derivative) was prepared by nitration of sodium *o*-nitrotoluene-ω-sulphonate with a hot mixture of sulphuric and nitric acids. The sodium salt crystallised in colourless leaflets and developed a green colour with cold, dilute aqueous sodium hydroxide; on heating, an intense bluish-green solution was obtained.

The authors wish to thank the Advisory Council of the Department of Scientific and Industrial Research for a grant that enabled one of them to take part in the investigation.

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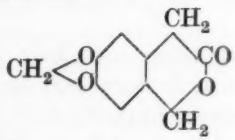
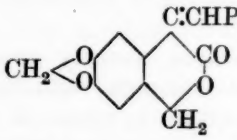
CCCLXXII.—*A New Synthesis of Hydrastic Acid.*

By THOMAS STEVENS STEVENS and MARY CARRICK ROBERTSON.

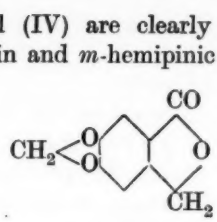
IN the course of recent synthetic work, the lactone (I) was obtained by the action of formaldehyde on homopiperonylic acid, and its structure confirmed by oxidising it to 4 : 5-methylenedioxyhomophthalic acid (Stevens, this vol., p. 178). It was further considered desirable to attempt the conversion of (I) into hydrastic acid, both on account of the interest attaching to a synthesis of that important substance, and also because the homophthalic acid is not readily characterised.

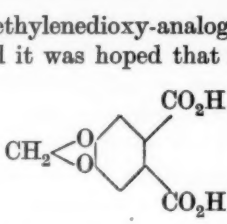
(I.) 

 (II.)

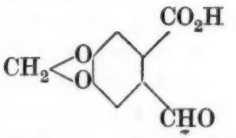
The compound (I) was condensed with benzaldehyde in presence of piperidine to form the lactone (II) of α-(6-*hydroxymethylpiperonyl*)-*cinnamic acid*. Oxidation with neutral permanganate converted this into 4 : 5-*methylenedioxyphthalide* (III), which was further oxidised in alkaline solution to hydrastic acid (IV). The substances

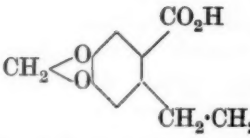
(III) and (IV) are clearly the "methylenedioxy-analogues" of *m*-meconin and *m*-hemipinic acid, and it was hoped that it would

(III.) 

(IV.) 

be possible to complete the series by oxidising (III) to the aldehydo-acid (V), analogous to *m*-opianic acid, but this could not be accomplished.

(V.) 

(VI.) 

The hydroxy-acid derived from the lactone (I) lactonises spontaneously when liberated from its salts, whereas that derived from (III), like many derivatives of *o*-hydroxymethylbenzoic acid, is comparatively stable. This greater stability of the γ-hydroxy-acids relatively to the δ-, as compared with the opposite behaviour of simple aliphatic compounds, is significant in view of von Braun's suggestion that in the formation of cyclic structures two carbon atoms of a benzene ring are sterically more nearly equivalent to one methylene group than to two (*Ber.*, 1925, **58**, 2765; 1927, **60**, 1257). On the other hand, 6-β-hydroxyethylpiperonylic acid (VI) (Perkin, J., 1890, **57**, 1020) and β-*o*-hydroxyphenylpropionic acid are fairly stable. The relative stabilities of these three δ-hydroxy-acids are in striking contrast to those of the δ-amino-acids prepared by von Braun and Reich (*Annalen*, 1925, **445**, 225), who observed that the lactam of *o*-aminomethylphenylacetic acid, analogous to (I), was *less* readily formed than those of the isomeric β-*o*-aminophenylpropionic and *o*-β-aminoethylbenzoic acids.

Experimental.

α-(6-*Hydroxymethylpiperonyl*)*cinnamolactone* (II).—The lactone (I) (10 g.) is dissolved in hot benzaldehyde (15 c.c.), piperidine (8—10 drops) added, and the mixture heated at 120° for 2 hours. The melt is dissolved in boiling acetic acid, and the solid (12 g.), which separates on cooling, recrystallised from alcohol or acetic acid. It forms pale yellow needles, m. p. 190—192°, fairly soluble in hot acetic acid and sparingly soluble in alcohol, and gives an intensely orange solution in concentrated sulphuric acid (Found: C, 72·9; H, 4·3. $C_{17}H_{12}O_4$ requires C, 72·9; H, 4·3%). It dis-

solves slowly in boiling aqueous alkali to a colourless solution: on acidification a colourless acid separates, which passes back into the lactone on being heated with dilute acids.

4 : 5-*Methylenedioxyphthalide* (III).—A solution of the lactone (II) (10 g.) in warm acetone (230—300 c.c.) is cooled (any crystallisation being disregarded), and stirred during the gradual addition of potassium permanganate (13 g.) and magnesium sulphate (13 g.) in warm concentrated aqueous solution. The mixture is boiled and filtered; much of the product then separates on cooling, and more may be obtained from the manganese sludge (5 g. in all). Methylenedioxyphthalide is soluble in about 100 parts of boiling water, and crystallises in white needles, m. p. 188—189°, which sublime readily without decomposition at about 150—160°. The sublimate consists principally of stout, short prisms which show the same m. p. as the original material and are reconverted into the needles on crystallisation from water (Found: C, 60·6; H, 3·7. $C_9H_6O_4$ requires C, 60·6; H, 3·4%). Attempts to oxidise the substance to the aldehydo-acid (V) with manganese or lead dioxide and sulphuric or acetic acid, or with chromic anhydride in acetic anhydride, were not successful.

6-*Hydroxymethylpiperonylic Acid*.—The phthalide (III) is not attacked by cold carbonates, but rapidly dissolves in hot sodium hydroxide solution, and the hydroxy-acid is precipitated in minute crystals when the cold solution is acidified. It melts indefinitely at about 140—150°, quickly resolidifies, and then melts at the m. p. of the lactone (Found: *M*, by titration, 193. $C_9H_8O_5$ requires *M*, 196). The acid is readily soluble in hot water and crystallises unchanged on rapid cooling; boiling dilute mineral acids reconvert it at once into the lactone. The *silver* salt forms colourless, microscopic prisms which are sparingly soluble in boiling water (Found: Ag, 35·8. $C_9H_7O_5Ag$ requires Ag, 35·6%).

Hydrastic Acid (IV).—The phthalide (III) was dissolved in dilute alkali solution and oxidised in the cold with a moderate excess of aqueous potassium permanganate. On acidification of the filtrate from the manganese dioxide, hydrastic acid, m. p. 175° (decomp.), crystallised in a yield of more than 50% of the theoretical. It was characterised by conversion into the methylimide, m. p. 228°, and by analysis of the silver salt (Found: Ag, 51·0. Calc., Ag, 50·9%).

UNIVERSITY OF GLASGOW. [*Received, September 15th*, 1927.]

CCCLXXIII.—*The Action of Tolylhydrazines upon Dihydroxytartaric Acid.*

By Frederick Daniel Chattaway and William Gerald Humphrey.

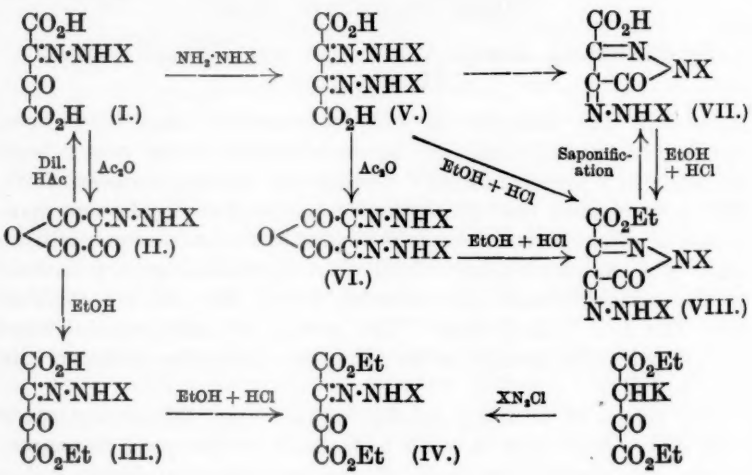
Although the osazones of dihydroxytartaric acid have been thoroughly investigated, its monohydrazones have never been prepared in a pure condition. Gnehm and Benda (*Annalen*, 1897, 299, 100) showed that the action of *p*-nitrophenylhydrazine upon excess of dihydroxytartaric acid yielded the pure osazone with no trace of a monohydrazone, whilst phenylhydrazine gave a mixture of the monohydrazone and osazone, which they did not separate into the two constituents. The action of halogen-substituted phenylhydrazines results in the formation of similar mixtures (this vol., p. 1323).

The action of *o*- and *p*-tolylhydrazines upon dihydroxytartaric acid differs from that of other hydrazines in that pure monohydrazones are readily obtained. These are well-crystallised, yellow solids, which, like the corresponding osazones, are converted into deep red acid anhydrides on heating with acetic anhydride. On crystallising these anhydrides from dilute acetic acid, the original hydrazones are re-formed; similarly, on crystallising the anhydrides from anhydrous alcohol, half-esters are formed. The second carboxyl group undergoes esterification only with difficulty, requiring prolonged boiling with alcohol containing hydrogen chloride; the diethyl ester thus formed may also be obtained by coupling diazotised toluidine with the potassium derivative of ethyl oxalacetate.

The most important property of the osazones of dihydroxytartaric acid is the ease with which they lose a molecule of water to give pyrazoline derivatives. This property is completely absent from the monohydrazones, and all attempts to cause pyrazoline ring formation have been unsuccessful.

The *o*- and *p*-tolylosazones of dihydroxytartaric acid behave in the normal manner. They are sparingly soluble substances which cannot be crystallised unchanged from any solvent. They are converted into deep red anhydrides by heating with acetic anhydride, and into hydrazones of diketopyrazolinecarboxylic acids by crystallisation from acetic acid or by acidification of their sodium salts. In the former reaction, varying amounts of the isomeric anhydrides are simultaneously produced. These pyrazoline derivatives undergo esterification with difficulty and their esters are more easily obtained from the corresponding osazone.

The following scheme represents the reactions, X denoting the tolyl group:



EXPERIMENTAL.

Diketosuccinic acid o-*tolylhydrazone* (I) was prepared by adding a solution of 26 g. of sodium dihydroxytartrate (1 mol.) in 180 c.c. of moderately concentrated hydrochloric acid (1 : 1) to a solution of 16 g. of *o*-tolylhydrazine hydrochloride (1 mol.) in 1000 c.c. of very dilute hydrochloric acid (1 : 100). The *hydrazone* separated slowly as a deep yellow, crystalline powder, which was filtered off after 3—4 hours and crystallised from 75% acetic acid, in which it was moderately easily soluble and from which it separated in yellow, elongated, flat prisms, m. p. 192° (decomp.) (Found: N, 11·2. $C_{11}H_{10}O_5N_2$ requires N, 11·2%).

This hydrazone shows no tendency to lose water to form a pyrazoline derivative. It dissolves readily in hot sodium hydroxide solution and is reprecipitated on acidification. On boiling with acetic acid, partial conversion into the anhydride occurs, whilst boiling with alcohol containing hydrogen chloride causes esterification only.

Anhydrodiketosuccinic Acid o-*Tolylhydrazone* (II).—The hydrazone (I) was added to boiling acetic anhydride until no more would dissolve. A clear, deep red solution was thus obtained which on cooling deposited the *anhydride* in long, red, glistening prisms, m. p. 208° (decomp.) (Found: N, 12·2. $C_{11}H_8O_4N_2$ requires N, 12·1%).

Ethyl Hydrogen Diketosuccinate o-*Tolylhydrazone* (III).—The

above anhydride was boiled with anhydrous alcohol and the yellow solution thus obtained, on cooling, deposited the half-ester in yellow, irregular, thin plates, m. p. 115° (Found : N, 9·9. $C_{13}H_{14}O_5N_2$ requires N, 10·1%).

The half-ester may also be prepared by boiling the hydrazone (I) with alcohol containing 5% of dry hydrogen chloride for ½ hour.

A definite formula cannot be assigned to this ester, as there is nothing to indicate which of the two carboxyl groups is esterified. The product appears not to be a mixture; its melting point is not changed by recrystallisation, and the fact that the second group can be esterified only with great difficulty points to a particular one being concerned in the first reaction.

Ethyl Diketosuccinate o-*Tolylhydrazone* (IV).—Although one carboxyl group of diketosuccinic acid *o*-tolylhydrazone is readily esterified, the diethyl ester was formed only by boiling the half-ester for 12 hours with alcohol saturated with dry hydrogen chloride. A certain amount of decomposition and tar formation occurred, and a dark brown solution was obtained, which on cooling deposited the *diethyl* ester in bright yellow, hexagonal plates or flattened prisms, m. p. 90° (Found : N, 9·1. $C_{15}H_{18}O_5N_2$ requires N, 9·15%).

The same ester was prepared by adding slowly a cold aqueous solution of *o*-toluenediazonium chloride (1 mol.) to an aqueous solution of the potassium derivative of ethyl oxalacetate (1 mol.), cooled in a freezing mixture. A sticky, red mass separated, from which, by crystallisation from alcohol, ethyl diketosuccinate *o*-tolylhydrazone was obtained, identical with that prepared by direct esterification.

Diketosuccinic acid o-*tolylosazone* (V) was prepared by adding a solution of 26 g. of sodium dihydroxytartrate (1 mol.) in 180 c.c. of moderately concentrated hydrochloric acid (1 : 1) to a solution of 32 g. of *o*-tolylhydrazine (2 mols.) in 1500 c.c. of dilute hydrochloric acid (1 : 100). The mixture was stirred for 6 hours and heated at 80° for 2 hours. The *osazone* was filtered off without previous cooling, repeatedly washed with boiling water, and dried at 110°. It was thus obtained as an orange powder, m. p. 170° (decomp.) (Found : N, 15·6. $C_{18}H_{18}O_4N_4$ requires N, 15·8%).

Anhydrodiketosuccinic Acid o-*Tolylosazone* (VI).—The osazone (V) was added to boiling acetic anhydride until no more would dissolve. On cooling, the *anhydride* separated in long, glistening, red prisms, m. p. 198° (decomp.) (Found : N, 16·6. $C_{18}H_{16}O_3N_4$ requires N, 16·7%).

4 : 5-*Diketo*-1-o-*tolylpyrazoline*-3-*carboxylic acid* 4-o-*tolylhydrazone* (VII) is formed together with the isomeric anhydride (VI) on crystallising the osazone (V) from acetic acid. It is, however,

best obtained by acidifying the orange-coloured solution produced by dissolving the osazone in hot 10% sodium hydroxide solution; the *tolylhydrazone* thus obtained separates from acetic acid, in which it is sparingly soluble, in very small, yellow prisms, m. p. 229° (decomp.) (Found: N, 16·45. $C_{18}H_{16}O_3N_4$ requires N, 16·7%).

Its *ethyl* ester (VIII), obtained by boiling the osazone (V), the anhydride (VI), or the pyrazolone (VII) with alcohol containing 5% of dry hydrogen chloride, crystallises from alcohol, in which it is easily soluble, in long, orange-red prisms, m. p. 145° (Found: N, 15·5. $C_{20}H_{20}O_3N_4$ requires N, 15·4%).

The following derivatives of *p*-tolylhydrazine were similarly prepared.

Diketosuccinic acid p-*tolylhydrazone* (I) is moderately easily soluble in 75% acetic acid, from which it separates in orange-yellow octahedra, m. p. 190° (decomp.) (Found: N, 11·3%). The *anhydride* (II) crystallises from acetic anhydride in deep red, elongated prisms, m. p. 192° (decomp.) (Found: N, 12·1%). The *half-ester* (III) is easily soluble in alcohol, from which it separates in lemon-yellow, slender prisms, m. p. 112° (Found: N, 10·05%).

Diketosuccinic acid p-*tolylosazone* (V) was obtained as a soft, orange-red powder, m. p. 175° (decomp.) (Found: N, 15·65%). The *anhydride* (VI) forms red, elongated prisms, m. p. 230° (decomp.) (Found: N, 16·5%).

4 : 5-*Diketo*-1-p-*tolylpyrazoline*-3-*carboxylic acid* 4-p-*tolylhydrazone* (VII) is sparingly soluble in acetic acid, from which it separates in very small, pale yellow prisms, m. p. 233° (decomp.) (Found: N, 16·7%). Its *ethyl* ester (VIII) is easily soluble in alcohol, from which it separates in orange-red, slender prisms, m. p. 143° (Found: N, 15·55%).

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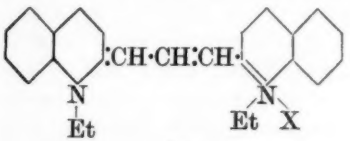
CCCLXXIV.—*A General Method for the Preparation of Carbocyanine Dyes.*

By FRANCES MARY HAMER.

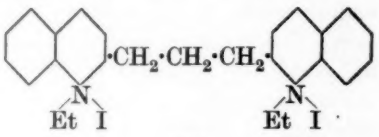
SINCE 1920, when the term "carbocyanine" was first applied to pinacyanol and similar dyes (Mills and Pope, *Phot. J.*, 1920, **44**, 253), other types of compounds have been discovered which, from their structure and properties, should be included under the same name. Before describing the present general method of preparing carbocyanines, it seems desirable to summarise these various types

and the methods which have hitherto been employed in making them.

The most important carbocyanine dye is 1 : 1′-diethyl-2 : 2′-carbocyanine halide (I), which, under the trade name of pinacyanol, is a well-known photographic sensitiser. Hitherto the best way of preparing it has consisted in adding formaldehyde and then alkali to a boiling alcoholic solution of a quinaldinium salt in the presence of a quinolinium salt, but the yield of pure dye is at most only 21% of that theoretically possible. The part played by formaldehyde may be taken by a trihalogenomethane (D.R.-P., 200,207/1908), or the methenyl residue may be provided by di-*o*-formylethylaminodiphenyl disulphide, reacting with quinaldine ethonitrate in pyridine solution (Mills and Braunholtz, J., 1923, **123**, 2804). König obtained pinacyanol by the condensation of quinaldine ethiodide with ethyl orthoformate in the presence of acetic anhydride (*Ber.*, 1922, **55**, 3293), but his claim to a 50% yield could not be confirmed (Hamer, J., 1925, **127**, 211). Finally, the dye has been derived from methylenediquinaldine diethiodide (II) by the action of alkali

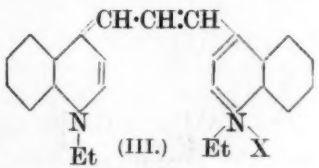


(I.)

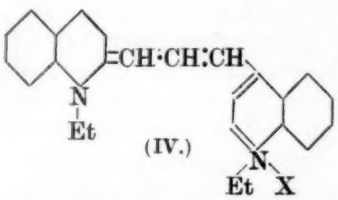


(II.)

in the presence of a quinolinium salt (Hamer, J., 1923, **123**, 246). The establishment of the constitution of pinacyanol (Mills and Hamer, J., 1920, **117**, 1550) led to the prediction of two similar groups of carbocyanines, possessing respectively a 4 : 4′- and a 2 : 4′-linking (III and IV) in place of the original 2 : 2′-linking. Mills and Braunholtz (*loc. cit.*) prepared a dye of the first type (III)



(III.)

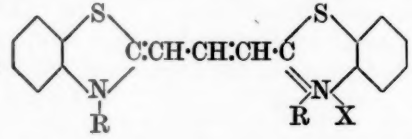


(IV.)

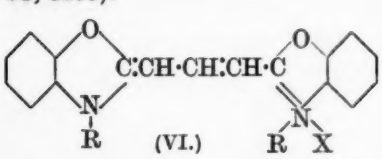
from lepidine ethonitrate by the action of the disulphide and pyridine, and showed the corresponding iodide, obtainable in 15% yield, to be identical with "kryptocyanine," which had previously been prepared, in 9% yield, by treating an alcoholic solution of lepidine ethiodide with alkali and formaldehyde or chloroform (Adams and Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661). Mills

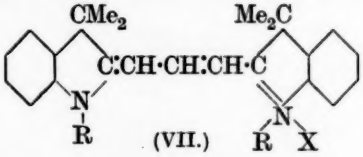
and Odams similarly synthesised the 2 : 4′-isomeride (IV) by the action of the disulphide on the ethonitrates of quinaldine and lepidine, and proved "dicyanine" to be a dye of this kind (J., 1924, **125**, 1913).

Besides these three closely related classes of carbocyanines, analogous dyes are obtained when the quinoline nuclei are replaced by other basic nuclei. Mills has shown that the dyes formed by the action of ammonia on the quaternary salts of 1-methylbenzthiazole and benzthiazole (Hofmann, *Ber.*, 1887, **20**, 2262) result in better yield (19%) when the salts are heated in pyridine solution, and has proved that they have formula (V) (J., 1922, **121**, 455). Substances of the same class were prepared by König and Meier,

(V.) 

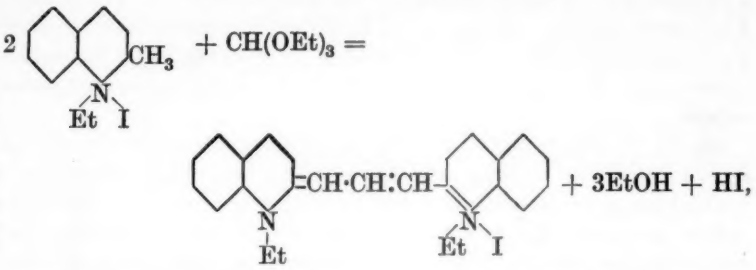
by condensation of 1-methylbenzthiazole methohalide with ethyl orthoformate, or anhydrous sodium formate, in nitrobenzene solution; they mention that the reaction proceeds equally well in acetic anhydride or pyridine solution (*J. pr. Chem.*, 1925, **109**, 324). Repetition of the preparation of the methobromide in nitrobenzene solution, or of the methiodide in acetic anhydride solution, has been found to give unsatisfactory results. By heating 1-methylbenzoxazole methiodide with ethyl orthoformate in the presence of nitrobenzene or acetic anhydride, König and Meier prepared a dye of a new type (VI) (*loc. cit.*), whilst König prepared another class of carbocyanine (VII) by treatment of a 2 : 3 : 3-trimethylindoleninium salt with ethyl orthoformate and acetic anhydride (*Ber.*, 1924, **55**, 3293).


(VI.)


(VII.)

As regards the nomenclature of these last three groups of carbocyanine dyes, the term *thiocarbocyanine* is preferred to the name carbothiocyanine (Mills, *loc. cit.*), as being more consistent with the terms thio*iso*cyanine (Braunholtz and Mills, J., 1922, **121**, 2004), thio*pseudo*cyanine (Mills and Braunholtz, *loc. cit.*), and pyridocarbocyanine (*ibid.*). It is proposed that the dyes (VI) and (VII), derived from benzoxazole and indolenine, be named *oxacarbocyanines* and *indocarbocyanines* respectively.

Now the equation representing the reaction of quinaldine ethiodide



with ethyl orthoformate suggests that the pinacyanol condensation would be favoured by the use of a basic solvent. Boiling pyridine proved in fact to serve excellently, and to its use is attributable the whole success of the present method. The only precaution necessary is that of drying the solvent, whilst about four times the calculated quantity of ester should be taken. Three 2 : 2′-carbocyanines have been prepared by the pyridine method, the yields of pure product varying from 70 to 79%, and the method was subsequently applied to the preparation of carbocyanines of the other five classes. With the 2 : 4′-carbocyanines, the yield of crude material is higher and the labour involved is less than in any other published method of preparing dicyanines; their separation, by fractional crystallisation, from the 2 : 2′- and 4 : 4′-isomerides was not, however, carried out. The success of the method is especially striking in the case of the 4 : 4′-carbocyanines, the yields being 36 to 43% of the theoretical. In the preparation of 1 : 1′-diethyl-4 : 4′-carbocyanine iodide, there is formed in addition about half its amount of another dye, which may readily be isolated by virtue of its slight solubility. Its properties show it to be identical with " neocyanine," which has been described as a by-product in the preparation of kryptocyanine by the formaldehyde method, and which is a powerful sensitiser for the deep red and infra-red (Dundon, Schoen, and Briggs, *J. Opt. Soc. Amer.*, 1926, **12**, 397). The pyridine method is at its best in the case of the thiocarbocyanines, giving between 79 and 83% yields of pure dyes; with the oxacarbocyanines the yields are about 40% and with the indocarbocyanines about 70% of those theoretically obtainable.

It is concluded that the introduction of pyridine as solvent converts the synthesis of carbocyanines, by condensation of ethyl orthoformate with quaternary salts containing reactive methyl groups, into an excellent practical and general method of preparation; this is not only the simplest method to apply, but gives, in any and every instance, the best yield obtainable. The following

carbocyanines are now described for the first time: 6 : 6′-*dimethyl*-1 : 1′-*diallyl*-2 : 2′-*carbocyanine iodide* and *bromide*, 1 : 1′-*dimethyl*-4 : 4′-*carbocyanine iodide*, 1 : 1′-*diallyl*-4 : 4′-*carbocyanine iodide*, 2 : 2′-*diallylthiocarbocyanine bromide*, 2 : 2′-*diethyloxacarbocyanine iodide*, and 3 : 3 : 3′ : 3′-*tetramethyl*-1 : 1′-*diethylindocarbocyanine iodide*.

Mr. O. F. Bloch has examined the absorption spectra of all the dyes in alcoholic solution and tested their sensitising action, both by bathing plates in a solution and by adding the dye to the emulsion before coating. He has found that the indocarbocyanines and oxacarbocyanines are, like other cyanine dyes, photographic sensitisers, and it seems remarkable that their photographic properties have not previously been recorded. In the experimental section of this paper the photographic action is described only in those instances where this has not previously been done.

So far no carbocyanine containing two pyridine nuclei has been isolated, though Mills and Braunholtz (*loc. cit.*) attributed to a 2 : 2′-carbocyanine of this type absorption bands which they detected in the pyridine reaction mixture of 2-methylpyridine ethonitrate and di-*o*-formylethylaminodiphenyl disulphide. It is now found that a 2 : 2′-pyridocarbocyanine is not formed by condensation of 2-methylpyridine ethiodide with ethyl orthoformate in the presence of boiling pyridine, a negative result which is curious in view of the readiness with which 2-methylpyridine quaternary salts condense with *p*-nitrosodimethylaniline (Kaufmann and Vallette, *Ber.*, 1912, **45**, 1736) and with *p*-dimethylaminobenzaldehyde (Mills and Pope, J., 1922, **121**, 946).

Experimental.

1 : 1′-*Diethyl*-2 : 2′-*carbocyanine Iodide*.—Quinaldine ethiodide (5 g.; 2 mols.), ethyl orthoformate (5·5 c.c.; 4 mols.), and pyridine (20 c.c.), which had been dried by being left over barium oxide and subsequent decantation, were boiled under reflux for 3 hours; crystals then separated (yield 78%). After recrystallisation from dilute spirit, the yield was 70%. The dye was dried under reduced pressure at 100—120° and an iodine determination was made by the method of Carius; these methods of drying and analysis were used in all cases, except where otherwise stated (Found: I, 26·2. Calc. for $C_{25}H_{25}N_2I$: I, 26·4%).

6 : 6′-*Dimethyl*-1 : 1′-*diallyl*-2 : 2′-*carbocyanine Iodide*.—By heating 2 : 6-dimethylquinoline (5 g.; 1 mol.) and allyl iodide (3·4 c.c.; 1·2 mols.) in a sealed tube at 100° for 48 hours, extracting the product with ether, and recrystallising the residue from spirit, a 72% yield of 2 : 6-*dimethylquinoline alliodide* was obtained, in yellow crystals,

m. p. 198—199° (decomp.) (Found: I, 39·2. $C_{14}H_{16}NI$ requires I, 39·05%). The condensation of the alliodide (5 g.) with ethyl orthoformate was carried out as in the previous preparation and the product was washed with ether (yield 82%) and recrystallised from methyl alcohol (yield, 71%). It melts with decomposition at 280—281° (Found: I, 23·5. $C_{29}H_{29}N_2I$ requires I, 23·85%). In spirit solution there are absorption maxima at λ 5700 Å. and λ 6200, of which the latter is the stronger. When the dye is added to the emulsion the sensitising maxima lie at λ 5800 and λ 6450 and there is considerable fog. The fog is less when the plate is bathed in a solution of the dye, and the sensitising action is considerably greater, the principal band now extending from λ 6200 to λ 7300.

6 : 6′-*Dimethyl*-1 : 1′-*diallyl*-2 : 2′-*carbocyanine Bromide*.—A 76% yield of 2 : 6-*dimethylquinoline allobromide* is obtained by heating 2 : 6-dimethylquinoline (7 g.; 1 mol.) and allyl bromide (6·2 c.c.; 1·2 mols.) in a sealed tube at 100° for 48 hours and recrystallising the product from absolute alcohol. It is a colourless solid, m. p. 214—215° (decomp.) (Found: Br, 28·9. $C_{14}H_{16}NBr$ requires Br, 28·7%). Its condensation with ethyl orthoformate in the presence of pyridine gave an 84% yield of carbocyanine (14·6 g.) and on recrystallisation from methyl alcohol a 79% yield of pure dye. This forms green and gold crystals, m. p. 281—282° (decomp.) (Found: Br, 16·5. $C_{29}H_{29}N_2Br$ requires Br, 16·5%).

1 : 1′-*Dimethyl*-4 : 4′-*carbocyanine Iodide*.—This compound is mentioned in the literature (Adams and Haller, *loc. cit.*), but none of its properties has been recorded. After condensation of lepidine methiodide (1 g.) with ethyl orthoformate in the presence of pyridine, the reaction mixture was poured into water; a 71% yield of crude product then resulted. From methyl alcohol it separated in minute, bright green crystals (yield 38%), m. p. 290—295° (decomp.) (Found: I, 28·0. $C_{23}H_{21}N_2I$ requires I, 28·1%). The dye shows an absorption maximum at λ 7150. The sensitising action towards plates on bathing is poor and is accompanied by veil; the single sensitising band has its maximum at λ 7500. When the dye is added to the emulsion, the sensitising action is less but the fog greater.

1 : 1′-*Diethyl*-4 : 4′-*carbocyanine Iodide* (*Kryptocyanine*).—After the condensation of lepidine ethiodide with ethyl orthoformate in the usual way, the reaction mixture was cooled and filtered (0·89 g. removed); on addition of water to the filtrate, the kryptocyanine was precipitated (2·23 g., *i.e.*, 56% of the theoretical yield). The kryptocyanine was recrystallised from spirit (150 c.c.); the yield (1·67 g.) was then 42% (Found: I, 26·4. Calc. for $C_{25}H_{25}N_2I$: I, 26·4%). The less soluble neocyanine iodide also was recrystallised

from spirit (1000 c.c.; 0·72 g. obtained). When heated, it melts with decomposition at 286°.

1 : 1′-*Diallyl*-4 : 4′-*carbocyanine Iodide*.—Lepidine (3·9 c.c.; 1 mol.) and allyl iodide (3·2 c.c.; 1·2 mols.) were heated in a sealed tube at 100° for 2 days. The *lepidine alliodide* was recrystallised twice from dry spirit, charcoal being used once (Found: I, 40·8. $C_{13}H_{14}NI$ requires I, 40·8%). The condensation product from lepidine alliodide (1 g.) and ethyl orthoformate was precipitated as a tar on the addition of ether to the pyridine reaction liquid. Rapid crystallisation from a little methyl alcohol gave a 43% yield of green crystals, but the carbocyanine was unstable and decomposed on prolonged boiling with the solvent. When heated, decomposition began at about 150° (Found: I, 25·6. $C_{27}H_{25}N_2I$ requires I, 25·2%). The maximum absorption in spirit solution is at λ 7150. On a bathed plate, the dye confers a strong sensitisation band with its maximum at λ 7550. The band occupies the same position when the dye is added to the emulsion, but is in this case much weaker.

2 : 2′-*Dimethylthiocarbocyanine Iodide*.—Repetition of the preparation using ethyl orthoformate and acetic anhydride gave only 17% and 9% yields of crude and recrystallised dye respectively. By the new method, 1-methylbenzthiazole methiodide (4 g.; 2 mols.), pyridine (40 c.c.), and ethyl orthoformate (4·6 c.c.; 4 mols.) were boiled for an hour. The thiocarbocyanine (yield, 95%) was recrystallised from dilute spirit and obtained in 74% yield. Melting with decomposition occurs at about 280°; König and Meier (*loc. cit.*) give m. p. 254° (Found: I, 27·1. Calc. for $C_{19}H_{17}N_2IS_2$: I, 27·3%).

2 : 2′-*Diethylthiocarbocyanine Iodide*.—This dye was similarly prepared from 1-methylbenzthiazole ethiodide (2 g.), and recrystallised from methyl alcohol (yield, 82%); m. p. 264—265° (decomp.); Mills (*loc. cit.*) gives m. p. 269° (decomp.) (Found: I, 25·6. Calc. for $C_{21}H_{21}N_2IS_2$: I, 25·8%).

2 : 2′-*Diallylthiocarbocyanine Bromide*.—By heating 1-methylbenzthiazole (6·3 g.; 1 mol.) with allyl bromide (3·5 c.c.; 1·2 mols.) in a sealed tube at 100° for 48 hours and recrystallising the product from spirit, 1-*methylbenzthiazole allobromide* was obtained in almost colourless crystals (yield, 68%), m. p. 202° (decomp.) (Found: Br, 29·8. $C_{11}H_{12}NBrS$ requires Br, 29·6%). The crude dye (yield, 95%), obtained on condensation of 1-methylbenzthiazole allobromide (2 g.) with ethyl orthoformate, was recrystallised from methyl alcohol; the pure thiocarbocyanine (yield, 79%) forms purple crystals, m. p. about 260° (decomp.) (Found: Br, 17·0. $C_{23}H_{21}N_2BrS_2$ requires Br, 17·0%). In spirit solution, the stronger absorption band has its maximum at λ 5600 and the weaker at λ 5220. As used in the emulsion, the dye is a powerful sensitiser;

there is a strong band with its maximum at λ 6000 and a weaker one with a maximum at λ 5450. It acts as an excellent sensitiser when plates are bathed in its solution, the sensitisation being almost uniform up to λ 6200 and decreasing to zero at λ 6800; there is a slight gap at λ 4900.

2 : 2′-*Dimethyloxacarbocyanine Iodide.*—1-Methylbenzoxazole could not be obtained by interaction of *o*-aminophenol and ethyl acetate (Niementowski, *Ber.*, 1897, **30**, 3062), but was prepared by Ladenburg's method (*Ber.*, 1876, **9**, 1524). The methiodide, after being washed with dry ether as described by Clark (J., 1926, 232), was rapidly recrystallised from absolute alcohol; the colourless crystals obtained were washed with ether and dried in a vacuum desiccator before analysis (Found: I, 46·1. Calc. for $C_9H_{10}ONI$: I, 46·15%). M. p. 196° (decomp.) as recorded by Clark; König and Meier (*loc. cit.*) give m. p. 200°. 1-Methylbenzoxazole methiodide (2 g.; 2 mols.), ethyl orthoformate (3·0 c.c.; 4 mols.), and pyridine (20 c.c.) were boiled for an hour. The dye (yield, 57%) was recrystallised from absolute alcohol (yield, 40%). The yield is about half as great when acetic anhydride is used as solvent in the condensation. The oxacarbocyanine has m. p. 275—277° (decomp.); König and Meier give m. p. 259° (Found: I, 29·2. Calc. for $C_{19}H_{17}O_2N_2I$: I, 29·4%). The absorption maxima in spirit solution lie at λ 4850 and λ 4600, of which the former is the stronger. When added to the emulsion, the dye confers a region of extra sensitivity with a maximum at λ 5100. Both in this case and with the bathed plate the sensitisation curve is very uniform, reaching to λ 5700 for moderate exposures.

2 : 2′-*Diethyloxacarbocyanine Iodide.*—1-*Methylbenzoxazole ethiodide* was prepared by heating 1-methylbenzoxazole (5·5 g.; 1 mol.) and ethyl iodide (4·0 c.c.; 1·2 mols.) in a sealed tube at 100° for 48 hours. After extraction with dry ether, the crude product was rapidly recrystallised from absolute alcohol, washed with ether, and dried for analysis in a vacuum desiccator (yield, 74%); the colourless crystals thus obtained had m. p. 195—197° (decomp.) (Found: I, 43·7. $C_{10}H_{12}ONI$ requires I, 43·9%). Condensation of the ethiodide (8 g.) with ethyl orthoformate gave 2 : 2′-*diethyloxacarbocyanine iodide* (yield, 57%), which crystallised from pyridine, in 38% yield, in red crystals with a blue reflex; m. p. 277—279° (decomp.) (Found: I, 27·5. $C_{21}H_{21}O_2N_2I$ requires I, 27·6%). The absorption maxima in spirit solution are at λ 4600 and λ 4850, of which the latter is the stronger. For bathing plates the dye acts as a powerful sensitiser, extending the normal sensitivity by a band which shows a maximum at λ 5150. Its action is weaker when it is added to the emulsion.

1 : 3 : 3 : 1′ : 3′ : 3′-*Hexamethylindocarbocyanine Iodide.*—In this instance the yield obtained by using acetic anhydride as solvent is equal to that which results when pyridine is employed. 2 : 3 : 3-Trimethylindolenine methiodide (2 g.; 2 mols.), pyridine (20 c.c.), and ethyl orthoformate (3·0 c.c.; 4 mols.) were boiled for an hour and the reaction mixture was poured into water. The crude product (yield, 78%) gave on recrystallisation from dilute or dry spirit, acidified with hydrogen iodide, a 66% yield of beautifully crystalline dye, but the iodine content was invariably low (*e.g.*, a specimen which had been dried in a vacuum desiccator gave C, 60·6; H, 6·5; I, 24·0. Calc. for $C_{25}H_{29}N_2I$: C, 61·95; H, 6·0; I, 26·2%. $C_{25}H_{29}N_2I,C_2H_5{\cdot}OH$ requires C, 61·1; H, 6·65; I, 23·9%). The indocarbocyanine has m. p. about 228° (decomp.); König (*loc. cit.*) gives m. p. 229° (decomp.). The absorption maxima lie at λ 5120 and λ 5480. When added to the emulsion, the dye gives very clean plates and shows fair sensitising action; the maxima lie at λ 5320 and λ 5720. When plates are bathed in a solution of the dye, the sensitisation is very powerful, and maxima occur at λ 5300 and λ 5800.

3 : 3 : 3′ : 3′-*Tetramethyl*-1 : 1′-*diethylindocarbocyanine Iodide.*—Trimethylindolenine ethiodide has been previously prepared by the action of methyl iodide on 2-methyl-1-ethylindole (König and Müller, *Ber.*, 1924, **57**, 144), but in the present work it was obtained by heating 2 : 3 : 3-trimethylindolenine (8·2 g.; 1 mol.) and ethyl iodide (5 c.c.; 1·2 mols.) in a sealed tube at 100° for 48 hours. After recrystallisation from rectified spirit, the ethiodide (yield, 61%) had m. p. 224° (decomp.) (Found: I, 40·2. Calc. for $C_{13}H_{18}NI$: I, 40·3%). The crude carbocyanine (yield, 86%), obtained by condensation with ethyl orthoformate, was recrystallised from dilute spirit acidified with hydrogen iodide, and was obtained in 75% yield. It forms pleochroic crystals, which are olive-green and steel-blue. If rapidly heated, it softens at 204—210°, or, if slowly heated, melts and resolidifies; it melts at 260—263° (decomp.) (Found: I, 24·8. $C_{27}H_{33}N_2I$ requires I, 24·8%). In spirit solution, the chief absorption maximum occurs at λ 5480 and there is a weaker band with its maximum at λ 5120. When added to the emulsion, the dye shows moderate sensitising action and has three maxima, at λ 5350, 5750 and 6000, respectively. In sensitising by bathing, it shows two maxima, at λ 5320 and λ 5700, and its action is more powerful.

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CCCLXXV.—*Quaternary Salts in the Benzselenazole Series.*

By LESLIE MARSHALL CLARK.

THE zinc salt of *o*-aminoselenophenol, which reacts with benzoyl chloride to give phenylbenzselenazole (Bauer, *Ber.*, 1913, **46**, 92), reacts similarly with formic acid to give *benzselenazole* (I).

(I.) $C_6H_4<^{Se}_{N}>CH$ $\qquad$ $\left[C_6H_4<^{Se}_{NMe\cdot CHO}\right]_2$ (II.)

Benzselenazole methiodide, when titrated in aqueous solution with sodium hydroxide and phenolphthalein, requires two equivalents of alkali for neutralisation. The neutral solution reduces one equivalent of iodine, a compound, $(C_8H_8ONSe)_2$, being formed. This behaviour of benzselenazole methiodide is clearly analogous to that of benzthiazole methiodide (Mills, Clark, and Aeschlimann, J., 1923, **123**, 2353) and must be ascribed to formation of the carbinol base, subsequent opening of the heterocyclic ring to give the sodium salt of *o*-formylmethylaminoselenophenol, $CHO\cdot NMe\cdot C_6H_4\cdot SeNa$, and oxidation of this by iodine (or other mild oxidising agents) to *di-o-formylmethylaminodiphenyl diselenide* (II).

Similar reactions occur when 2-phenylbenzselenazole methiodide is treated with two equivalents of sodium hydroxide, followed by one of iodine, and are, therefore, probably general for all 2-alkyl- and 2-aryl-substituted benzselenazolinium salts.

Atmospheric oxidation of benzselenazole methiodide in ammoniacal solution gives *di-o-methylaminodiphenyl diselenide*, the formyl groups of (II) having been removed by contact with ammonium hydroxide. Similar treatment of benzthiazole methiodide gives di-*o*-formylmethylaminodiphenyl disulphide, di-*o*-methylaminodiphenyl disulphide being produced only when sodium hydroxide is substituted for ammonium hydroxide (compare Mills, Clark, and Aeschlimann, *loc. cit.*).

Confirmation of the correctness of the explanations advanced above is obtained by the benzoylation of the di-*o*-methylaminodiphenyl diselenide obtained from benzselenazole methiodide. The product is identical with the compound obtained from 2-phenylbenzselenazole methiodide by treatment with alkali and oxidation.

During the preparation of benzselenazole, *di-o-formylaminodiphenyl diselenide* was isolated as a by-product. This compound, when treated in alcoholic solution with stannous chloride, gave some benzselenazole by preliminary reduction to *o*-formylaminoselenophenol, which then underwent condensation by loss of water.

The formyl groups in di-*o*-formylaminodiphenyl diselenide are readily removed by heating with phenylhydrazine, since α-formylphenylhydrazine is obtained from the reaction mixture.

Experimental.

The zinc salt of *o*-aminoselenophenol was prepared by Bauer's method (*loc. cit.*), but a better yield (56%) of di-*o*-aminodiphenyl diselenide was obtained by oxidising the solution of *o*-aminoselenophenol, well stirred and cooled below 6°, with potassium ferricyanide instead of hydrogen peroxide.

Benzselenazole (I).—The zinc salt of *o*-aminoselenophenol (17 g.) was boiled during 14 hours with anhydrous formic acid (140 c.c.), and the solution poured into water; a light-coloured oil, which rapidly solidified, was then precipitated. Excess of ammonium hydroxide was added and the oily suspension and the solid deposit (A) were extracted by means of ether. The extract was dried over sodium carbonate, the solvent removed, and the residue distilled, giving *benzselenazole* (4·5 g.), a slightly yellow liquid, b. p. 154°/45 mm., having an odour very similar to that of benzthiazole (Found : N, 8·0. C_7H_5NSe requires N, 7·7%).

Benzselenazole Methiodide.—A mixture of the base (4·2 g.) and methyl iodide (5 g.) was kept for 24 hours and then heated on the water-bath for 3 hours. The resulting solid, after being washed with ether, crystallised from alcohol in very pale yellow needles (yield, 80%), m. p. 188—189° (Found : C, 29·4; H, 2·45; N, 4·2; I, 39·1; Se, 24·1. C_8H_8NISe requires C, 29·6; H, 2·5; N, 4·3; I, 39·2; Se, 24·4%). *Benzselenazole methopicrate*, obtained from the methiodide and picric acid in alcoholic solution, had m. p. 173° (Found : N, 12·8. $C_{14}H_{10}O_7N_4Se$ requires N, 13·2%).

Action of Sodium Hydroxide on Benzselenazole Methiodide.—Benzselenazole methiodide (1·500 g.) in aqueous solution required 9·3 c.c. of 1·02*N*-sodium hydroxide for neutralisation (Calc. for two equivs. of NaOH, 9·1 c.c.). On oxidation of the cold solution with potassium ferricyanide a yellowish, oily substance was precipitated. This was extracted with benzene, and the extract was dried over sodium carbonate and concentrated, and light petroleum added until a permanent turbidity appeared; *di-o-formylmethylaminodiphenyl diselenide* (II) slowly separated in small, colourless prisms, m. p. 104° (Found : C, 45·0; H, 3·8; N, 6·7; *M*, cryoscopic in camphor, 424. $C_{16}H_{16}O_2N_2Se_2$ requires C, 45·1; H, 3·75; N, 6·6%; *M*, 426).

Oxidation of o-*Formylmethylaminoselenophenol by Iodine.*—Benzselenazole methiodide (0·3240 g.), dissolved in water, was treated with two equivalents of sodium hydroxide. The slightly yellow solution required 9·3 c.c. of *N*/10-iodine for oxidation (Calc. for 1 equiv.,

10·0 c.c.). The error in the titration is undoubtedly due to atmospheric oxidation, which appears to be more rapid in the case of the selenophenols than in that of the thiophenols. Di-*o*-formylmethylaminodiphenyl diselenide, m. p. 104°, was isolated as before.

Atmospheric Oxidation of o-*Formylmethylaminoselenophenol.*—Benzselenazole methiodide (0·3 g.) was dissolved in water (30 c.c.), and ammonium hydroxide (2 c.c.; *d*, 0·880) added. The solution became yellow and slightly turbid; after it had been kept for several hours in the dark, a crystalline, yellow substance separated on the surface. If the concentration of ammonium hydroxide was greater than that stated, the crystals were accompanied by a yellow oil. When the solution had lost its yellow colour, the crystals were removed and purified by evaporation of a solution in light petroleum. After several repetitions of this procedure, *di-o-methylaminodiphenyl diselenide* was obtained, m. p. 89° (Found: C, 45·3; H, 4·2; N, 7·5. $C_{14}H_{16}N_2Se_2$ requires C, 45·4; H, 4·3; N, 7·6%). This diselenide is very readily soluble in organic solvents. It separates from ether in yellow, hexagonal tablets, very similar in appearance to those of di-*o*-methylaminodiphenyl disulphide (Mills, Clark, and Aeschlimann, *loc. cit.*).

Di-*o*-methylaminodiphenyl diselenide (0·2 g.), shaken with benzoyl chloride and sodium hydroxide, gave a pasty mass; after crystallisation from aqueous alcohol, this had m. p. 170°, alone or when mixed with di-*o*-benzoylmethylaminodiphenyl diselenide obtained from 1-phenylbenzselenazole methiodide (see below).

1-*Phenylbenzselenazole Methiodide.*—1-Phenylbenzselenazole (2 g.), prepared by Bogert and Chen's method (*J. Amer. Chem. Soc.*, 1922, 44, 2355), was heated at 100° during 26 hours with methyl iodide (2·5 c.c.). After removal of the excess of methyl halide, the residue was extracted with ether to remove unchanged base. The crude *methiodide* crystallised from alcohol in golden-yellow needles, m. p. 211—212° (decomp.) (Found: I, 31·5. $C_{14}H_{12}NISe$ requires I, 31·75%). 1-*Phenylbenzselenazole chloroplatinate* was prepared from alcoholic-hydrochloric acid solutions of the base and platinic chloride and separated in flattened, yellowish-brown needles [Found: Pt, 20·8. $(C_{13}H_9NSe)_2H_2PtCl_6$ requires Pt, 21·0%].

Action of Sodium Hydroxide on 1-*Phenylbenzselenazole Methiodide: Di-*o*-benzoylmethylaminodiphenyl Diselenide.*—The methiodide (0·210 g.), dissolved in water, was titrated at 50° with sodium hydroxide and phenolphthalein. The addition of each portion of alkali caused the transient red coloration of the indicator which is characteristic of pseudo-base formation (Required: 19·3 c.c. of *N*/20-sodium hydroxide. Calc. for two equivs., 19·5 c.c.). This solution, cooled and titrated with 0·0625*N*-iodine, required 7·0 c.c. for complete

oxidation, whereas the amount calculated for one equivalent of iodine is 8·4 c.c. This discrepancy must again be ascribed to atmospheric oxidation. The colourless solid, *di*-o-*benzoylmethylaminodiphenyl diselenide*, which separated after the iodine oxidation crystallised from aqueous alcohol in stout needles, m. p. 170° (Found : C, 58·4; H, 4·1; N, 5·1; Se, 27·0. $C_{28}H_{24}O_2N_2Se_2$ requires C, 58·1; H, 4·15; N, 4·8; Se, 27·3%).

Di-o-*formylaminodiphenyl Diselenide*.—The deposit A, obtained from the formylation of *o*-aminoselenophenol, crystallised from alcohol (charcoal) in soft, pale yellow needles, m. p. 174°. Analysis showed it to be *di*-o-*formylaminodiphenyl diselenide*, which must have been produced by atmospheric oxidation of aminoselenophenol to the corresponding diselenide, followed by formylation of the amino-groups (Found : C, 42·4; H, 3·1; N, 7·0. $C_{14}H_{12}O_2N_2Se_2$ requires C, 42·2; H, 3·0; N, 7·0%).

Preparation of Benzselenazole from Di-o-*formylaminodiphenyl Diselenide*.—The diselenide (1·8 g.), dissolved in alcohol–acetone, was reduced with excess of stannous chloride in dilute hydrochloric acid solution. The mixture was heated at 100° for ½ hour and then evaporated to dryness. The residue was treated with sodium hydroxide solution and the oil liberated was taken up in ether, dried over sodium carbonate, and distilled in a vacuum. The distillate was heated with excess of methyl iodide at 70—80° for 4 hours, the uncombined methyl iodide boiled off, and the partly crystalline residue dissolved in acetone; on addition of ether to this solution a crystalline deposit was formed which, after purification, melted at 187°, alone or when mixed with authentic benzselenazole methiodide.

Reaction between o-*Diformylaminodiphenyl Diselenide and Phenylhydrazine*.—The diselenide (0·5 g.) was heated with phenylhydrazine (1·2 g.) at 100° for 3 hours and the orange-red oil produced was cooled and diluted with ether; colourless plates of α-formylphenylhydrazine were deposited; these, after crystallisation from water, had m. p. 144°, alone or when mixed with an authentic specimen.

A satisfactory method for the estimation of selenium in organic compounds of the type described in this paper is as follows : The compound is decomposed by treatment with 50 c.c. of 8% potassium permanganate solution and 10 c.c. of concentrated nitric acid. The mixture is evaporated to dryness on the steam-bath, 10 c.c. of the permanganate solution and 5 c.c. of nitric acid are added to the residue, and the evaporation is repeated. The addition of permanganate and acid and the evaporation are repeated, 80 c.c. of concentrated hydrochloric acid are added to the residue, and the

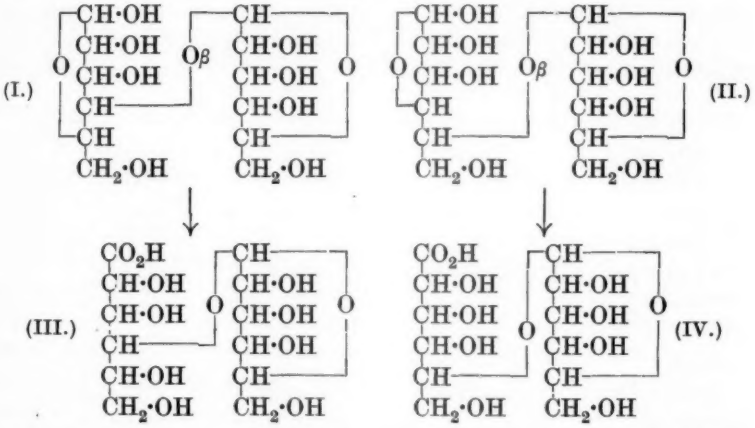
mixture is boiled until chlorine and nitric acid are removed. The solution is then diluted and selenium determined by reduction with sulphurous acid.

22 STANLEY ROAD, TEDDINGTON. [*Received, October 6th*, 1927.]

CCCLXXVI.—*The Constitution of the Disaccharides. Part XVI. Cellobiose.*

By WALTER NORMAN HAWORTH, CHARLES WILLIAM LONG, and JOHN HERBERT GEOFFREY PLANT.

A CONSTITUTIONAL study of cellobiose was undertaken in this series (Part V) six years ago (Haworth and Hirst, J., 1921, **119**, 193), and the experimental results were as follows: Methylated cellobiose ⟶ crystalline tetramethyl glucose + crystalline 2 : 3 : 6-trimethyl glucose; and a structural formula was ascribed to the disaccharide on this basis. In common with all carbohydrate formulæ, this constitution was modified by the recognition of the revised formula of glucose in its normal derivatives (Charlton, Haworth, and Peat, J., 1926, 98), and the structure represented by (I) was assigned to cellobiose by the latter authors:

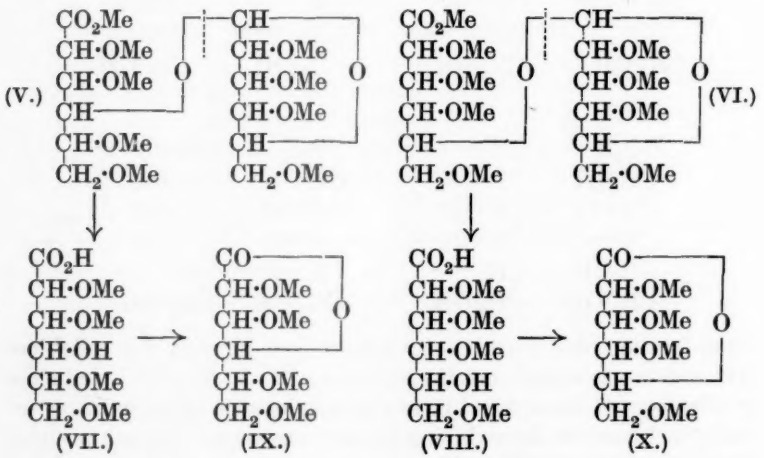


Consideration was given to an alternative formula for cellobiose (II), and it was stated that the isolation of 2 : 3 : 6-trimethyl glucose by cleavage of methylated cellobiose rendered it possible to regard the attachment of the reducing hexose component through position (5) to the other hexose residue, in which case the oxide ring of this first residue would be a butylene or γ-oxide (1 : 4) and not an amylene or δ-oxide (1 : 5). In the former case, cellobiose would be

to the extent of one residue a γ-sugar, but this was stated to be an unlikely contingency. Whilst making this reservation, therefore, the formula (I) for cellobiose was advocated, inasmuch as it correctly represented the properties of the disaccharide and was consistent with all the facts.

Meanwhile, we have instituted a series of experiments designed to eliminate any remaining doubt as to the structure of cellobiose. This disaccharide undergoes oxidation at its reducing position to give a monobasic acid designated cellobionic acid, and this compound can be formed only by opening of the ring of the reducing glucose component. The structure of cellobionic acid will thus be represented by formula (III) if (I) be accepted for the disaccharide, whilst (IV) will represent the acid if (II) be the structure of the disaccharide. It will therefore be seen that, in the two rival formulæ for the acid, the position of the oxygen link connecting the two C_6 chains differs in that in (III) this link engages the carbon in position (4), and in formula (IV) it engages the carbon in position (5).

We have been able to decide between these two alternative formulæ by methylating cellobionic acid completely, and the product, which was *methyl octamethylcellobionate*, was then submitted to hydrolysis. The cleavage products to be expected are seen to be different according as we accept formula (V) or formula (VI) as a correct representation of the methyl octamethylcellobionate. In addition to 2 : 3 : 4 : 6-tetramethyl glucose, the cleavage products



should contain a monobasic acid of the C_6 series which, if formula (V) be correct, would be the γ-hydroxy-acid (VII); or if formula (VI)

be correct, the δ-hydroxy-acid (VIII). Since each of these acids is already known and has been fully characterised by one of us in earlier investigations, a way was opened up enabling us to reach a decision through identification of this essential product. It will be seen that an acid of formula (VII) would give on heating a 1 : 4- or γ-lactone, recognisable as 2 : 3 : 5 : 6-tetramethyl gluconolactone, and similarly an acid of formula (VIII) would yield a 1 : 5- or δ-lactone, identifiable as 2 : 3 : 4 : 6-tetramethyl gluconolactone; and since each of these lactones has been fully characterised and degraded by oxidation methods (Haworth, Hirst, and Miller, this vol., p. 2436), there can be no dubiety in assigning a final constitution to each of them, and therefore to cellobiose itself.

When methyl octamethylcellobionate was hydrolysed with mineral acid, the cleavage products were isolated in an analogous manner to that described in recent papers on maltose (Haworth and Peat, J., 1926, 3094) and lactose (Haworth and Long, this vol., p. 544). Crystalline 2 : 3 : 4 : 6-tetramethyl glucose was isolated (yield, 92·7% of the theoretical), and the acid product originally retained as the barium salt was regenerated and distilled as a lactone which crystallised, m. p. 26—27° (yield, 80% of the theoretical). This compound gave a phenylhydrazide of the corresponding acid, m. p. 135—136°, and the melting point was not depressed in admixture with the phenylhydrazide of 2 : 3 : 5 : 6-tetramethyl gluconic acid which had been prepared from (*a*) methyl octamethyl-maltobionate or methyl octamethyl-lactobionate or (*b*) 2 : 3 : 5 : 6-tetramethyl γ-glucose (1 : 4) (compare Haworth and Long, Haworth and Peat, *locc. cit.*).

Again, the above lactone was shown to be identical with 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone isolated from the sources (*a*) and (*b*). There was, therefore, no doubt that the tetramethyl gluconic acid which had been formed from methyl octamethylcellobionate was that represented by formula (VII), since the lactone referred to is indicated by formula (IX). The results furnish evidence which seems to us conclusive in favour of the formulation (V) for methyl octamethylcellobionate, and therefore, if this be accepted, and it be assumed that no displacement of the biose linking had occurred in any of these transformations, cellobionic acid should be expressed by formula (III) and cellobiose by (I). This experimental result substantiates the constitutional formula which had previously been advocated by one of us and serves to remove the need for any reservation in favour of formula (II).

It should be noted in this connexion that, as indicated by Haworth and Peat (*loc. cit.*), maltose possesses the same structural formula as

cellobiose, the essential difference between these two bioses being that maltose is a glucose-α-glucoside and cellobiose a glucose-β-glucoside.

These experimental results are opposed to the views of Irvine (*Chemical Reviews*, 1927, **4**, 216), who has perceived a difference in the positions of (*a*) the biose linking in maltose and cellobiose and (*b*) the oxide ring in each of these bioses (compare Irvine and Black, J., 1926, 869; Irvine and Macdonald, *ibid.*, 1508; Irvine and Robertson, *ibid.*, 1496).

Experimental.

Cellobiose octa-acetate (m. p. 223—225°), prepared as described by Haworth and Hirst (J., 1921, **119**, 193) from pure cellulose, was hydrolysed by alcoholic potash to give potassium cellobiosate, and a representative sample of the latter was converted into cellobiose having $[\alpha]_D$ +24° ($c = 3{\cdot}33$) (equilibrium value) (Maquenne, *Bull. Soc. chim.*, 1904, **31**, 854). The remaining portion of potassium cellobiosate was dissolved in a little water, and bromine was admitted, which speedily dissolved. The solution was kept in a stoppered bottle at room temperature for 10 days; it was then almost devoid of reducing action towards Fehling's solution. The unchanged bromine was removed by aeration, followed by treatment with hydrogen sulphide. The colourless solution was shaken with finely ground litharge, filtered, then agitated in presence of silver oxide in the dark, and filtered. Hydrogen sulphide was again passed into the solution, and the excess of this gas removed by aeration. The clear solution was warmed gently for a day in presence of calcium carbonate, filtered, and evaporated to small bulk. This contained calcium cellobionate along with potassium bromide.

Methyl Octamethylcellobionate.—The methylation of calcium cellobionate was carried out in a similar manner to that described in the case of the corresponding salt of maltobionic acid (Haworth and Peat, *loc. cit.*), methyl sulphate and sodium hydroxide being used initially, followed by several treatments with moist silver oxide and methyl iodide, and finally by dry silver oxide and methyl iodide. The crude product at this stage was a yellow, mobile liquid (7·1 g.; OMe, 54·6%). This distilled under 0·05 mm. from a bath heated to 203°, and the first fraction (1·5 g.) of low boiling point was rejected. The major portion of the distillate (5·1 g.) was a pale yellow, viscid syrup, $n_D^{13^\circ}$ 1·4604 (Found: OMe, 54·3%). The latter was again distilled under 0·05 mm., the first fraction (0·3 g.) being collected on heating the bath to 176°, and the main fraction (4·6 g.) distilled at 169—171°/0·05 mm. from a bath heated

to 192°. This product did not reduce Fehling's solution and had $n_D^{14°}$ 1·4609, and the analytical data agreed with the formula of *methyl octamethylcellobionate* (Found: C, 52·0; H, 8·3; OMe, 54·3. $C_{21}H_{40}O_{12}$ requires C, 52·1; H, 8·3; OMe, 57·6%).

Hydrolysis. The above product (3·1 g.) was dissolved in 100 c.c. of 7% hydrochloric acid, and heated at 80—90° until the specific rotation of the solution appeared to show no further changes. $[\alpha]_D^{19°}$ + 5·4° (initial), + 32·1° (after 1 hour), 50·2° (2 hours), 54·6° (3 hours), 55·0° (4 hours; constant). At this stage finely divided barium carbonate was gradually added, and the solution aerated at 50° to assist the neutralisation. After being kept over-night, the solution was filtered and evaporated at 40°/16 mm. To the white residue, alcohol was added and distilled off under 16 mm. The dry solid was digested with boiling ether many times and the collected extracts were evaporated, leaving a syrup which crystallised in colourless needles. These were purified from light petroleum (weight, 1·5 g.; yield, 92·7%) and identified as 2 : 3 : 4 : 6-tetramethyl glucose by the following properties: m. p. 93—94°; mixed m. p. determination with a specimen prepared from methylated maltose, 93—94°; $[\alpha]_D^{14°}$ in water (c = 2·02) + 99·9° (5 mins.), 88·0° (30 mins.), 85·5° (1 hour), 83·0° (2 hours; constant).

The original white residue of barium salts from which the tetramethyl glucose had been extracted was warmed to eliminate traces of ether, dissolved in water, and treated with a slight deficiency of dilute hydrochloric acid. The water was evaporated at 50°/15 mm. and finally the residue was heated at 60—80°/0·09 mm. for 2 hours. Repeated digestion of this dried residue with boiling ether yielded 1·2 g. (80% of the theoretical) of a pale yellow syrup which distilled under 0·09 mm. from a bath heated to 119°, leaving only 0·1 g. of residue.

Nucleation of the cooled distillate with 2 : 3 : 5 : 6-tetramethyl gluconolactone (from methyl octamethyl-lactobionate; Haworth and Long, this vol., p. 547) resulted in immediate crystallisation; m. p. 26—27°, mixed m. p. determination 26—27° (with the specimen from which the nucleus had been taken) (Found: C, 51·2; H, 7·8; OMe, 51·4. Calc.: C, 51·3; H, 7·7; OMe, 53·0%).

Phenylhydrazide of 2 : 3 : 5 : 6-*Tetramethyl Gluconic Acid.*—A specimen of the above lactone (0·16 g.) in contact with phenylhydrazine (1 mol.) dissolved in ether was heated on a water-bath. Crystals of the phenylhydrazide separated, m. p 135—136° (from benzene), mixed m. p. 135—136° [with specimens prepared from the 2 : 3 : 5 : 6-tetramethyl gluconolactone obtained from methyl octamethylmaltobionate (Haworth and Peat, *loc. cit.*) and from 2 : 3 : 5 : 6-tetramethyl (γ-)glucose (Charlton, Haworth, and Peat, *loc. cit.*)]

(Found: C, 56·1; H, 7·65; OMe, 35·0; N, 8·45. Calc.: C, 56·1; H, 7·6; OMe, 36·3; N, 8·2%).

The authors are indebted to the Department of Scientific and Industrial Research for grants to two of them.

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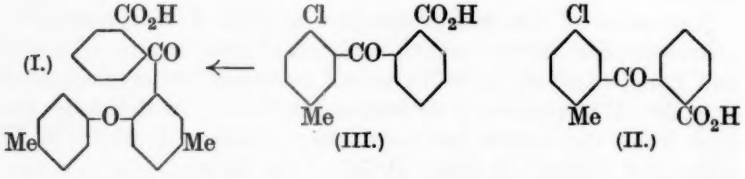
CCCLXXVII.—*Substituted Diaryl Ethers. Part II. The Friedel–Crafts Reaction applied to Di-*p*-tolyl Ether.*

By JOSEPH REILLY and PETER J. DRUMM.

ALTHOUGH there are two similar benzene nuclei in di-*p*-tolyl ether in both of which substitution may occur, the authors find that this ether yields only monoketonic derivatives in the Friedel–Crafts reaction. The condensation of di-*p*-tolyl ether proceeds more readily with phthalic anhydride than with benzoyl chloride, substitution occurring in one position only; from benzoyl chloride more than one substance appears to be formed.

Condensation of 2-hydroxy-5-methylbenzophenone-2′-carboxylic acid with *p*-bromotoluene gives 2-*o*-*carboxybenzoyldi*-p-*tolyl ether* (I), identical with the product of interaction between phthalic anhydride and di-*p*-tolyl ether. The formation of a 2-ketone in the latter reaction is what would be expected and is in line with the authors' recent work on the nitration of di-*p*-tolyl ether (this vol., p. 68) showing that the oxygen atom exerts the main orienting influence.



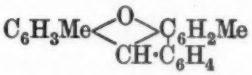
The substance (I) has also been obtained by condensing *p*-cresol with the chloromethylbenzophenone-*o*-carboxylic acid which Heller and Schulke (*Ber.*, 1908, **41**, 3627) prepared from *p*-chlorotoluene and phthalic anhydride. Their ketone therefore has formula (III), not (II), the chlorine atom exerting a greater directive influence than the methyl group.

The product obtained by heating (I) with concentrated sulphuric acid is, not an anthraquinone derivative, but 2 : 7-dimethylfluoran,

identical with that obtained by Drewsen (*Annalen*, 1882, **212**, 341) from phthalic anhydride, *p*-cresol, and sulphuric acid; it gives 2 : 2′-dihydroxy-5 : 5′-dimethylbenzophenone and benzoic acid on fusion with potassium hydroxide.

Although 2-*benzoyldi*-p-*tolyl ether* (formula as I) has not been directly synthesised, its constitution as an ortho-substituted diaryl ether is indicated by the following facts. Its solutions in acetic and sulphuric acids are yellow and fluorescent, indicating xanthhydrol formation through ring closure. From these solutions, 9-phenyl-2 : 7-dimethylxanthen was isolated identical with that obtained by Feuerstein and Lipp (*Ber.*, 1902, **35**, 3255) by the dry distillation of 6 : 6′-dihydroxy-3 : 3′-dimethyltriphenylmethane.

The conditions employed by Feuerstein and Lipp in preparing the phenyldimethylxanthen were so drastic that its constitution is not beyond doubt. Moreover, its formation from benzoyldi-*p*-tolyl ether in acetic acid—the change is more readily effected by boiling alcoholic hydrochloric acid—is difficult to understand. It seems to the authors that the substance may be a fluorene,



but to this view there is the objection that the molecule of such a substance would be in a state of considerable strain; the formula also shows linkage at a position (1 in the xanthen ring) which is not only sterically hindered but is also meta with respect to the oxygen atom. In support of the fluorene formula, however, may be quoted the following facts: (1) Phenyldi-α-naphthylcarbinol, on boiling with acetic acid, changes into phenyldi-α-naphthafluorene (Schoepfle, *J. Amer. Chem. Soc.*, 1922, **44**, 190); (2) Ullmann and Mourawiew-Winigradoff (*Ber.*, 1905, **38**, 2213), on heating diphenyl-α-naphthylcarbinol with an acetic acid solution of sulphuric acid, zinc chloride, or hydrochloric acid, obtained phenylchrysofluorene. In offering the above suggestion, it is appreciated that phenyl groups exhibit less tendency than naphthyl groups to formation of fluorene linkages.

It was not found possible to prepare the oxime from 2-*o*-carboxybenzoyldi-*p*-tolyl ether (I), and the phenylhydrazone was only obtained under drastic conditions. These appear to be cases of steric hindrance by substituents in the two ortho-positions with respect to the carbonyl group. 2-Benzoyldi-*p*-tolyl ether, under identical conditions, did not give a phenylhydrazone, the reaction proceeding in a different direction.

Contrary to the generally accepted view that the reaction between benzoyl chloride and phenols in presence of aluminium chloride

results in poor yields of hydroxybenzophenones unless the hydroxyl group has been previously protected (compare Fries and Finck, *Ber.*, 1908, **41**, 4276; Heller, *Ber.*, 1913, **46**, 1498), it is now found that with acetylene tetrachloride as solvent 2-hydroxy-5-methylbenzophenone is obtained in good yield from *p*-cresol and benzoyl chloride.

Experimental.

2-o-*Carboxybenzoyldi*-p-*tolyl Ether* (I).—A mixture of di-*p*-tolyl ether (8 g.) and phthalic anhydride (6 g.) was slowly added to anhydrous aluminium chloride (9 g.), covered with dry carbon disulphide and protected from moisture. After 12 hours, the product was poured on ice, the carbon disulphide and other volatile products were removed in steam, and the colourless residue was repeatedly dissolved in aqueous sodium hydroxide and precipitated by dilute acid. The product then crystallised from aqueous ethyl alcohol in long, hexagonal prisms (yield, 70%), m. p. 155° (Found : C, 76·2; H, 5·5; *M*, cryoscopic in naphthalene, 360. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2%; *M*, 346).

Repetition of the above experiment, twice the quantities of phthalic anhydride and aluminium chloride being used, gave the same product, namely, 2-o-*carboxybenzoyldi*-p-*tolyl ether*, in approximately the same yield, no diketonic derivative being isolated.

Synthesis of 2-o-*Carboxybenzoyldi*-p-*tolyl Ether*.—*p*-Bromotoluene (10 g.), the dipotassium derivative (10 g.; dried at 120° in a vacuum) of 2-hydroxy-5-methylbenzophenone-2′-carboxylic acid prepared by Ullmann's method (*Ber.*, 1919, **52**, 2102), and a trace of copper bronze (Naturkupfer C, washed with ether to remove oily impurities) were heated in absolute-alcoholic solution in a sealed tube for 10 hours at 200°. The product was distilled in steam; unchanged *p*-bromotoluene passed over, followed by di-*p*-tolyl ether (1 g.). The residual oil was extracted with hot dilute sodium hydroxide solution, the extract acidified, and the viscous precipitate obtained crystallised from acetic acid (80%); 2-*o*-carboxybenzoyldi-*p*-tolyl ether slowly separated in colourless prisms, m. p. 154—155°, identical with the ether described above.

2-*o*-Carboxybenzoyldi-*p*-tolyl ether is readily soluble in glacial acetic acid, absolute alcohol or ether and very sparingly soluble in light petroleum (b. p. 60—80°) or water. It dissolves in concentrated sulphuric acid to an orange solution exhibiting a greenish fluorescence; the colour is discharged on dilution with water. Its *silver* salt is sparingly soluble in water, but readily soluble in dilute aqueous ammonia (Found : Ag, 23·9. $C_{22}H_{17}O_4Ag$ requires Ag, 23·8%). The ether, on fusion with potassium hydroxide, is decom-

posed into di-*p*-tolyl ether and phthalic acid. It unites with anhydrous aluminium chloride to give an orange-coloured solid.

The formation of di-*p*-tolyl ether in the above reaction was at first suspected to result from hydrolysis of the 2-*o*-carboxybenzoyldi-*p*-tolyl ether formed, but on heating *p*-bromotoluene and alcoholic potassium hydroxide under identical conditions di-*p*-tolyl ether was isolated in small quantity.

2-*o*-Carboxybenzoyldi-*p*-tolyl ether was recovered unchanged after being heated with hydroxylamine hydrochloride in strongly alkaline solution for 8 hours on the water-bath. The *phenylhydrazone* was obtained only by heating the ether (1 mol.) and phenylhydrazine (2 mols.) for 3 hours at 160—170°. The cooled product was extracted with very dilute hydrochloric acid; from an alcoholic solution of the residue, the *phenylhydrazone* separated in pale yellow needles, m. p. 156° (Found: N, 6·6. $C_{28}H_{24}O_3N_2$ requires N, 6·4%).

Action of Sulphuric Acid on 2-o-*Carboxybenzoyldi*-p-*tolyl Ether.*—The ether (1 g.) and concentrated sulphuric acid (8 c.c.) were heated on a boiling water-bath for 3 hours. The solution was then cooled and mixed with ice, and the precipitate obtained was collected and digested with aqueous sodium hydroxide solution; the extract was purple, owing probably to the presence of an anthraquinone derivative. The part insoluble in alkali was crystallised from absolute ethyl alcohol, 2 : 7-dimethylfluoran being obtained in colourless, glistening prisms (yield, 90%), m. p. 254° (Drewsen, *loc. cit.*, gives m. p. 246°) (Found: C, 80·6; H, 5·1. Calc. for $C_{22}H_{16}O_3$: C, 80·5; H, 4·9%).

The nature of this substance was established by fusion with potassium hydroxide at 220—240°. The dark yellow aqueous extract of the product was acidified and then boiled with sufficient alcohol to give a clear solution; on standing, yellow needles of 2 : 2′-dihydroxy-5 : 5′-dimethylbenzophenone separated which, after one recrystallisation from alcohol, had m. p. 104—106°. Distillation in steam of the filtrate from the fusion product gave benzoic acid.

Equal weights of 2-*o*-carboxybenzoyldi-*p*-tolyl ether and phosphorus pentachloride were heated in benzene solution until evolution of hydrogen chloride ceased. To the cooled, light orange solution was added the same weight of anhydrous aluminium chloride; hydrogen chloride was then again evolved. The deep red solution was finally refluxed for a short time and poured on ice; the product, isolated in the usual way, was 2 : 7-dimethylfluoran.

Constitution of Heller and Schulke's Ketone (III).—A mixture of the potassium salt of Heller and Schulke's ketone (*loc. cit.*) (1 mol.),

potassium *p*-tolyloxide (1·5 mols.), *p*-cresol (solvent), and a trace of copper bronze was slowly heated, with stirring, to 200°; at 160° potassium chloride separated. After being heated for an hour at 190—200°, the product was dissolved in water, and the solution was extracted with ether, acidified, and extracted with chloroform. The chloroform was evaporated, and the residue dissolved in hot acetic acid (80%); 2-*o*-carboxybenzoyldi-*p*-tolyl ether slowly crystallised in short, colourless prisms, m. p. 153—154°.

2-*Benzoyldi*-p-*tolyl Ether* (formula as I).—The preparation from di-*p*-tolyl ether (7 g.), benzoyl chloride (5 g.), and aluminium chloride (12 g.) is very similar to that of the carboxylic acid (I) described above. The residue obtained after the steam-distillation set to a crystalline mass which separated from boiling, absolute ethyl alcohol in colourless, glistening rhombohedra (5·5 g.), m. p. 185—186° (Found: C, 83·1; H, 6·3. $C_{21}H_{18}O_2$ requires C, 83·4; H, 6·0%). A viscous oil (4 g.) obtained from the mother-liquor resisted all attempts to crystallise it.

A second experiment with di-*p*-tolyl ether (7 g.), benzoyl chloride (10 g.), and aluminium chloride (24 g.) was carried out under identical conditions, but the same monobenzoyl compound was obtained (7·8 g.) and no dibenzoyl compound was isolated.

2-*Benzoyldi*-p-*tolyl ether* is readily soluble in chloroform, acetone or benzene, much less soluble in ethyl alcohol, and insoluble in light petroleum (b. p. 60—80°). It dissolves in concentrated sulphuric acid to a bright yellow solution with a green fluorescence; dilution with water discharges the fluorescence but not the colour. It combines with anhydrous aluminium chloride to form a bright orange solid which immediately decomposes in contact with water.

Glacial acetic acid in contact with 2-benzoyldi-*p*-tolyl ether is coloured yellow; it becomes orange on heating and reddish-orange on boiling. On cooling, 9-phenyl-2 : 7-dimethylxanthen separates in colourless, glistening needles which, alone or mixed with an authentic specimen, melt at 195—196° (Found: by the micro-method, C, 87·8; H, 6·2; *M*, cryoscopic in camphor, 312. Calc. for $C_{21}H_{18}O$: C, 88·1; H, 6·3%; *M*, 286. Calc. for $C_{21}H_{16}O$: C, 88·7; H, 5·6%; *M*, 284). The same xanthen was obtained when 2-benzoyldi-*p*-tolyl ether was heated with phenylhydrazine at 160° for 2 hours.

2-*Hydroxy*-5-*methylbenzophenone*.—To *p*-cresol (10 g.) and benzoyl chloride (14·1 g.), dissolved in dry acetylene tetrachloride and protected from moisture, anhydrous aluminium chloride (26·7 g.) was added during 1 hour. The mixture was then heated for 4 hours at 100—110°, hydrogen chloride being copiously evolved. After cooling, the dark brown solution was poured into water, a dark oil

separating. On distillation in steam, acetylene tetrachloride passed over, followed slowly by a light yellow oil which quickly solidified and was highly pure 2-hydroxy-5-methylbenzophenone (yield, 80%), m. p. 84·5° (Cox, *J. Amer. Chem. Soc.*, 1927, **49**, 1029, gives m. p. 87°).

2-p-*Tolyloxy*-5-*methylacetophenone*, prepared in the usual manner, was obtained as a red oil which was purified by distillation; the fraction, b. p. 320—340°, set to a crystalline solid which separated from alcohol in colourless, glistening plates, m. p. 168° (Found: C, 79·6; H, 7·0; *M*, cryoscopic in naphthalene, 251. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%; *M*, 240). This ketone has the characteristic odour of acetophenone and is readily soluble in ether, benzene, or hot alcohol. It dissolves in sulphuric acid to a yellow solution.

Addendum.—Since the above work was completed, a paper by Rosenmund and Schulz has appeared (*Arch. Pharm.*, 1927, **265**, 308), in which it is stated that the reaction between phenols and acid chlorides with aluminium chloride in nitrobenzene solution, giving phenolic ketones, is of general applicability. The unique behaviour of nitrobenzene is ascribed to its solvent action on the aluminium chloride complexes. Monohydric phenols react readily except when the *p*-position to the hydroxyl group is occupied. We have observed that acetylene tetrachloride also can be used as solvent in the preparation of phenolic ketones, and this holds even when the *p*-position to the hydroxyl group is occupied (*e.g.*, the yield of 2-hydroxy-5-methylbenzophenone is 80%).

UNIVERSITY COLLEGE, CORK. [*Received, September 5th*, 1927.]

CCCLXXVIII.—*The Action of Alkalis on Clay.*

By HENRY BOWEN OAKLEY.

IN the study of the physical and chemical properties of soils, much attention has always been directed towards the clay fraction which, together with humus, is responsible for the colloidal properties of the soil, and is one of the most reactive components chemically.

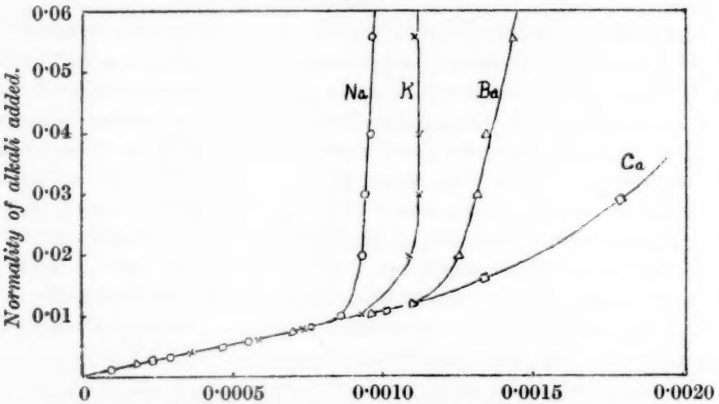
Although many diverse hypotheses have been put forward to account for the "absorption" of bases by clay, the trend of modern opinion is to regard the action as chemical in nature, being due to the formation of insoluble aluminosilicates, as opposed to the hypothesis of "physical absorption of ions," which is still largely adopted in many branches of colloid chemistry. The view that clay acts as a weak acid towards alkalis is supported by the electrometric titration curves of Bradfield (*J. Amer. Chem. Soc.*, 1923,

45, 2669), and is confirmed by the results presented in this paper. A fairly full bibliography on this subject is given by Bradfield (*J. Amer. Soc. Agronomy*, 1925, **17**, 253).

The clays used in this work were separated by sedimentation in 0·05% sodium carbonate, flocculated by dilute hydrochloric acid (N/100), and purified to a high resistance by dialysis (Joseph and Hancock, J., 1924, **125**, 1888).

The Effect of the Concentration of Alkali on the Amount of Base removed from Solution by Clay.—The clay used in these experiments was No. 10195 prepared from a heavy cotton soil: it was practically identical with No. 6640 (Joseph and Hancock, *loc. cit.*). 10 C.c. samples of a 5% suspension were treated with different

FIG. 1.



Equivalents of base taken up by 1 *g. of clay in the presence of* N/2*-chloride;* 1% *suspensions.*

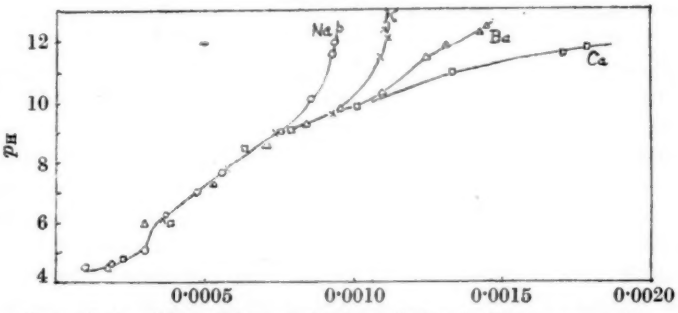
quantities of standard alkali in centrifuge tubes. Water and a standard chloride solution of the appropriate base were added to make the total volume 50 c.c. and N/2 with respect to the chloride. This treatment completely flocculated the clay. The tubes were centrifuged, and 25 c.c. of the clear, supernatant liquid were treated with excess of N/10-hydrochloric acid and titrated back with N/10-sodium hydroxide, as this procedure was found to give the sharpest end-point. Methyl-orange was used as indicator. A further portion was withdrawn for the p_H determination in a Clark cell with a Leeds and Northrup potentiometer. From the change in concentration of the alkali, the amount removed by the clay can be calculated, since any soluble silicates or aluminates which may be formed behave in titration as free alkali.

The results are illustrated in Figs. 1 and 2. The equivalents of base taken up per g. of clay are identical for sodium, potassium,

barium, and calcium up to an initial concentration of alkali of 0·01*N*, or an equilibrium p_H of about 9; but with a further increase in the concentration of alkali the amounts taken up are in the increasing order sodium, potassium, barium, and calcium. The amounts of sodium and potassium taken up attain fairly constant values above a p_H of 11, whereas barium and calcium show no such limit. This order is the same as that found for amorphous silica (Joseph and Oakley, J., 1925, **127**, 2813), and suggests that the quantity of any base retained in the solid phase is partly determined by the solubility or stability of the aluminosilicates and their products of decomposition with increasing concentrations of alkali.

The Total Amounts of Sodium and Calcium Hydroxides neutralised by Clay.—That the quantity of bases removed in the solid phase

FIG. 2.



Equivalents of base taken up by 1 g. of clay in the presence of N/2-chloride; 1% suspensions.

is closely connected with the solubility of the products of combination is illustrated by the following results for calcium and sodium hydroxides, giving the total amount of alkali neutralised in the two cases. No chloride was added in this experiment, and a lower concentration of clay was used so that the necessarily dilute calcium hydroxide could be present in a greater excess than in the previous experiment.

To determine the total sodium hydroxide neutralised, a series of p_H measurements was made on caustic soda solutions of various strengths; the hydroxyl-ion concentrations were then calculated by subtracting these values of the p_H from the values of Michaelis for $\log 1/K_w$ at the appropriate temperature (Clark, "The Determination of Hydrogen Ions," p. 29). These calculated values of the hydroxyl-ion concentrations were then plotted against the concentration of sodium hydroxide. In a similar manner, the concentration of hydroxyl-ions was calculated from the p_H of the clay suspensions. The corresponding concentration of sodium

hydroxide was read from the curve, and this value was subtracted from the original concentration of caustic soda added. The temperatures varied from 30° to 35°, but this was allowed for both in the calculation of the p_H and in the subsequent calculation. The error in the determination of the total hydroxide neutralised may be as much as 10%. An exactly similar method was applied for calcium. The results are in the following table (compare Bradfield, *Soil Sci.*, 1924, **17**, 411).

Total amount of calcium and sodium hydroxide neutralised by clay after standing 1 day. Concentration: 0·52% clay.

Initial conc. of hydroxide.	Equiv. of alkali neutralised per g. of clay.		Final p_H.	
	Sodium.	Calcium.	Sodium.	Calcium.
0·036	0·0018	0·0027	11·92	11·81
0·020	0·0012	0·0021	11·67	11·50
0·008	0·0010	0·0012	11·00	10·75

These results show that, although the total sodium hydroxide neutralised is about twice the amount taken up in the solid phase (compare Fig. 1), thus demonstrating the formation of soluble compounds, yet the amount of calcium hydroxide neutralised is still greater, although no soluble compounds are formed. This is shown by the fact that, for an initial calcium hydroxide concentration of 0·038 and a final p_H of 11·93, the amount of calcium hydroxide neutralised per g. of clay, as calculated from the p_H, was 0·0031, whereas that calculated from titration of the excess of alkali was 0·0032. (The concentration of the clay was 0·26%.)

The compounds formed by silica and calcium hydroxide were also found to be insoluble, but in this case they were equivalent in amount to the total sodium compounds formed under the same conditions (Joseph and Oakley, *loc. cit.*).

The influence of the concentration of the sodium on the amount of base taken up by 1 g. of clay is illustrated by the following figures with various concentrations of chloride:

Conc. of NaOH, 0·04*N*; conc. of clay, 1%.

Conc. of NaCl	1·0	0·5	0·2	0·1
Na taken up (equiv. × 10^4) ...	9·68	9·56	9·17	9·15
p_H	12·10	12·16	12·22	12·25

A comparison of the effect of *N*-solutions of chlorides on the amounts of sodium, potassium, and calcium taken up by 1 g. of clay is given in the following figures (equivs. × 10^4):

Chloride.	Concentration of hydroxide.		
	0·08*N*-NaOH.	0·08*N*-KOH.	0·03*N*-$Ca(OH)_2$.
0·0*N*	8·46	10·4	14·9
1·0*N*	9·60	12·8	17·8

As had been previously found with silica, the addition of the chloride of the base to an alkaline suspension always increased the amount of base taken up.

The removal of the base from solution by clay is very rapid. This is illustrated by the following figures for 1 g. of clay.

Conc. of NaOH, 0·04*N*; conc. of NaCl, 0·5*N*; conc. of clay, 1%.

Time	10 mins.	1 hr.	3 hrs.	1 day
Na taken up	9·7	9·9	9·8	10·3

The Relation between the Soluble and Insoluble Sodium Compounds with Clay.—In order to determine the relation between the soluble and the insoluble sodium compounds formed with increasing concentrations of sodium hydroxide, a series of 0·5-g. samples of clay was treated with different concentrations of standard caustic soda, the volume being always 50 c.c. After standing for 1 hour, 10 c.c. were withdrawn for a p_H determination. The remainder was filtered through a collodion filter and an aliquot portion of the clear filtrate was titrated with standard acid and alkali as before. The difference between the total amount neutralised (calculated from p_H) and the amount taken up (calculated from the titration) gave the equivalents of sodium neutralised in a soluble form. These results are in the following table.

The amounts of sodium neutralised in the solid phase and in solution by 1 g. of clay after 1 hour. Concentration of clay, 1%.

Initial conc. of NaOH.	p_H at equilibrium.	Equivs. Na in solid phase, × 10^4.	Equivs. Na neutralised in solution, × 10^4.	Ratio, Soluble/ Insoluble.
0·07	12·33	9·7	7	0·72
0·04	12·03	9·7	5	0·51
0·02	11·60	9·9	2	0·20
0·01	10·72	8·1	1	0·11
0·006	9·77	5·4	0·6	0·11
0·004	8·62	3·9	0·1	0·02

The amount of soluble sodium compounds formed is small until the p_H exceeds 10·5, or until the concentration of alkali is greater than 0·01*N*.* This is just the concentration at which the amounts of different bases taken up begin to diverge (Fig. 1). These results leave no doubt, I think, that the later process of the neutralisation of bases by clay at higher concentrations of hydroxide differs from the initial reaction at low concentrations, in that the more concentrated alkali begins to break down the clay substance, forming

* In the case of silica, the amount of sodium in the solid phase is always very small compared with the total silicate formed (J., 1925, **127**, 2816, Table IV).

silicates and aluminates. In the case of calcium, these are insoluble, and in the case of sodium, they are easily soluble, whilst potassium and barium occupy intermediate positions. In one special experiment, the amount of lithium taken up by 1 g. of clay in the presence of 0·5*N*-lithium chloride was $9{\cdot}0 \times 10^{-4}$ equiv. at a p_H of 9·8, and the amount for sodium under similar conditions was $9{\cdot}5 \times 10^{-4}$.

At the lower concentrations of alkali (below 0·01*N*), the identity of the amounts of different bases taken up shows that these solubility relationships do not come into play, the compounds formed with any of the bases being equally insoluble. In this case, there appears to exist a direct reversible equilibrium between these insoluble compounds and the bases in solution, the equilibrium with alkalis having characteristics similar to those of a weak acid in true solution; this is indicated by the shape of the curves for sodium in Figs. 2 and 4.

From these curves it is seen that the clay acid is half converted into its sodium compound at about p_H 8. If the laws of dissociation of a weak acid are applicable, this would mean that its dissociation constant is about 10^{-8}. Bradfield (*J. Physical Chem.*, 1924, **28**, 170), from the variation of the p_H with concentration of a clay suspension, calculated a value of 3×10^{-7}.

Further evidence that clay behaves as an insoluble acid in direct equilibrium with the bases in solution is afforded by the liberation of acid when a neutral salt is added to clay, and by the fact that clay so treated hydrolyses on being washed with water, giving an alkaline solution. The equivalence of the exchange of bases when clay is washed with the salt of another base also supports the view that the reactions are purely chemical in nature (*Trans. Faraday Soc.*, 1925, **22**, 251). The speed with which all these reactions take place and the influence of various electrolytes on the electrokinetic potential and stability of clay suspensions (Oakley, *J. Physical Chem.*, 1926, **30**, 902) seem to indicate that the reactions are mainly ionic. The fact that clay, with its weakly acidic properties, can remove some of the base from the salt of a strong acid, thus setting free this acid, also receives a natural explanation on the above view.

In order to determine the composition of the material dissolved from the clay, 5 g. of clay were shaken with *N*/10-sodium hydroxide in the presence of *N*/2-sodium chloride, the volume being adjusted so that the concentration of the clay was 1%. This was centrifuged and the clear supernatant liquid analysed for silica, alumina, and ferric oxide. This treatment was repeated four times for increasing periods of time with fresh additions of sodium hydroxide and chloride. Two further experiments were made with two separate

portions of the stock clay for periods of 1 hour and 3 days, respectively. The results are in the following table.

Material dissolved from 1 g. of clay by $N/10$-sodium hydroxide in the presence of $N/2$-sodium chloride. Concentration of clay (No. 14637), 1%.

A. Successive treatments on the same portion of clay.

Time.	SiO_2.	$Al_2O_3 + Fe_2O_3$.	$SiO_2/(Al_2O_3 + Fe_2O_3)$.
5 mins.	0·0050	0·0046	1·1
1 hour	0·0052	0·0020	2·6
1 day	0·0107	0·0018	6·0
3 days	0·0109	0·0017	6·4

B. Treatment on two separate portions of clay.

1 hour	0·0065	0·00466	1·41
3 days	0·0115	0·0044	2·62
Untreated clay	0·475	0·328	1·44

On the assumption that the soluble compounds formed are Na_2SiO_3 and $NaAlO_2$, the sodium so combined is $2·8 \times 10^{-4}$ and $4·4 \times 10^{-4}$ equiv., respectively, for the last two experiments (the ferric oxide also was estimated in these cases). The value obtained from p_H measurements after 3 days' standing was $4·5 \times 10^{-4}$, and the sodium removed in the solid phase was $7·6 \times 10^{-4}$. The figures in the last column show that the proportion of sesquioxides rapidly falls in successive treatments with caustic soda, there being a higher proportion of sesquioxides in the first extract than in the clay itself. Another notable result is that the amount of material dissolved increases very slowly on prolonging the time of contact of the alkali with the clay, and this independently of whether the clay has had previous treatments with caustic soda or not. These results suggest that the material which goes into solution strongly inhibits further solvent action of the alkali. Since the concentration of the sodium hydroxide is reduced only by about 15% in the case of the initial treatments, and by about 5% in the other cases, the decreased rate of solvent action is unlikely to be due to diminished alkali concentration.

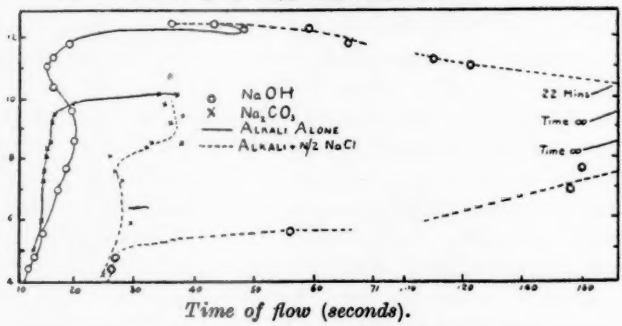
The Effect of Sodium Hydroxide and Sodium Carbonate on the Viscosity of Clay Suspensions.—It was thought that the difference in composition of the material removed by the early treatments compared with that from the later treatments might indicate that this material was identical with the hypothetical "layer of gel" on clay particles, which, according to some writers, gives clay its peculiar plastic and water-holding properties (*Brit. Assoc.*, 3rd Report on Colloid Chemistry, 1920, pp. 113—153).

If this is the case, the viscosity of clay in caustic soda solution of strength sufficient to dissolve this layer should be markedly less

than the value for clay in the presence of alkali too weak to dissolve the layer, since the particle size should be greatly reduced by the former treatment. Complicating factors in the comparison are the state of flocculation, and the state of saturation of the clay with regard to sodium. The times of flow of 10% suspensions of clay in an Ostwald viscometer were determined in a thermostat at 35°. One series of measurements was made on suspensions containing varying amounts of sodium hydroxide, and a similar series was made with sodium carbonate. After these measurements had been completed, sodium chloride was added in amount sufficient to make its concentration $N/2$. The times of flow of the deflocculated suspensions could be accurately repeated, but when the clay was flocculated, the time rapidly decreased with successive readings until an approximately constant value was reached, but this rose

FIG. 3.

Viscosity of 10% *clay suspensions.*



again on standing. The latter measurements are therefore very rough. The suspensions were too thick for the determination of their p_H; they were therefore diluted to one-fifth of their original concentration, and the p_H determinations were made on the diluted samples. If there was no buffer action, this dilution would decrease the p_H value by 0·7 unit, but since both the clay itself and the material dissolved by the alkali exert considerable buffer action, it is safe to conclude that the effect of dilution would not reduce the p_H by more than 0·3. The measurements were made on the suspensions after the addition of the sodium chloride.

The times of flow are plotted against the p_H in Fig. 3. The following data show the concentration of alkali added and the corresponding times of flow before the addition of sodium chloride. The time of flow of water was 10·4 seconds. [It is desirable to point out that the following figures cannot in any way be said to represent *true* viscosity values, for two reasons: (1) The rate of flow of the

uncoagulated suspensions was so high as to cause turbulent flow; and (2) Poiseuille's law is not obeyed by clay suspensions. Nevertheless, the results are of interest in showing that the comparative "thickness" of clay suspensions is affected differently by sodium hydroxide and by sodium carbonate.]

Conc. of NaOH or Na_2CO_3.	Time with NaOH (secs.).	Time with Na_2CO_3 (secs.).	Conc. of NaOH or Na_2CO_3.	Time with NaOH (secs.).	Time with Na_2CO_3 (secs.).
0·01	12·6	12·3	0·10	16·5	15·6
0·02	13·6	12·7	0·15	15·4	16·1
0·03	15·0	13·6	0·20	16·2	16·2
0·04	17·5	14·7	0·25	19·2	16·5
0·05	19·0	15·0	0·40	48·0	19·5
0·07	20·0	15·0	0·80	43·0	37·0
0·08	18·4	15·3			

The results show that at corresponding p_H values, the viscosity of clay treated with sodium carbonate is never greater than that of the clay treated with sodium hydroxide. The rapid rise in viscosity of the suspensions without sodium chloride at the highest values of the p_H is due to the flocculation of the clay by the alkali. Since the amount of material dissolved by the sodium hydroxide will be far greater than that dissolved by the sodium carbonate (carbonic acid being strong enough to decompose silicates and aluminates), it follows that this dissolved material cannot have existed in the clay in a particularly bulky and gelatinous condition. If this had been the case, its removal would have had a marked effect on the viscosity as compared with the values in the presence of sodium carbonate.

A striking feature of the results is that the curve for sodium hydroxide shows a maximum in viscosity between p_H 8 and 10, and this maximum is enormously enhanced when the clay is flocculated with sodium chloride. There is a complete absence of this effect with sodium carbonate, which suggests that it is connected with the much greater solvent power of the hydroxide. The hypothesis which accounts for the facts is that the sodium hydroxide at certain concentrations, instead of actually dissolving some of the clay, forms a comparatively non-viscous sol with this material. The addition of sodium chloride coagulates this sol, forming a coagulum of a very gelatinous nature. At higher concentrations of sodium hydroxide, this sol dissolves and cannot be coagulated by sodium chloride. This explains (1) why the maximum is only slight with caustic soda alone, but very pronounced in the presence of sodium chloride, (2) why the viscosity of the coagulated clay again falls when excess of caustic soda is added, and (3) why sodium carbonate does not show the effect.

This hypothesis is further supported by the fact that the clay

is more bulky with sodium hydroxide in the same range of p_H values at which the maximum in viscosity is observed, and that the maximum is not shown by sodium carbonate.

The following figures show the volume of 1 g. of clay (*i.e.*, of the clay plus its interstitial water after 10 minutes' centrifuging) after standing 1 day with various concentrations of alkali in the presence of $N/2$-sodium chloride.

Conc.	p_H with NaOH.	Vol., c.c.	p_H with Na_2CO_3.	Vol., c.c.	Conc.	p_H with NaOH.	Vol., c.c.	p_H with Na_2CO_3.	Vol., c.c.
0·0	4·0	4·1	—	—	0·1	12·3	5·1	8·3	4·1
0·02	7·6	4·6	—	—	0·2	12·9	4·7	8·8	4·3
0·03	8·0	5·4	—	—	0·3	13·1	4·4	9·0	4·2
0·04	9·5	5·7	—	—	0·5	13·3	4·2	10·2	4·3
0·05	11·1	5·5	8·1	4·0	1·0	13·6	4·1	10·4	4·5
0·07	12·2	5·3	—	—					

The fact that the clay without sodium hydroxide occupies the same volume as the clay in the presence of N-hydroxide affords further evidence that the material dissolved by the alkali is not specifically more bulky than the rest of the clay material.

Finally, the fact that the imbibitional water of the clay was unaltered by the prolonged treatment with sodium hydroxide points to the same conclusion. This water is the volume of water retained by 100 c.c. of the clay less the volume of xylene retained by the same clay after centrifuging for 40 minutes under a force of 1000 times gravity (compare Fisher, *J. Agric. Sci.*, 1924, **14**, 204). It was determined on the original clay (1) after drying with the addition of 9 c.c. of $N/10$-sodium hydroxide per g. of clay, and (2) on the clay left over after the four successive treatments with caustic soda described previously (p. 2825). This was washed until it was deflocculated and then collected on a collodion filter. Separate determinations were made, water and N-sodium chloride being used as the wetting liquids.

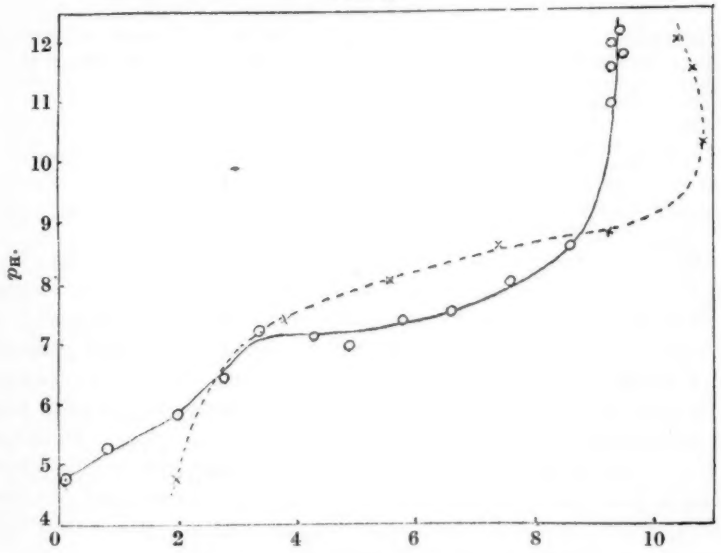
Imbibitional water of clay No. 14637.

	Water.	N-NaCl.
(1) 9×10^{-4} equiv. Na/g.	251	103
(2) Prolonged NaOH treatment	248	104

A Comparison of the Properties of a Synthetic Aluminosilicate and of Clays.—Although, in the comparison of different soil clays, some degree of correlation can be traced between base-absorbing capacity and certain colloidal properties such as heat of wetting, imbibitional water, and general clay-like properties, yet it is equally true that a substance having a composition similar to clay, a fair imbibitional water content, and a very large base-absorbing capacity may, nevertheless, show clay-like properties only to a very small

extent. This is well illustrated by the following experiments on a synthetic aluminosilicate. This was prepared (see de Sigmond, *Proc. 4th Inter. Confer. Pedology*, 1924, 2, 434) by mixing solutions of sodium aluminate and sodium silicate (both $N/10$ with regard to sodium; $Na_2O : SiO_2 = 1 : 2$) in such proportion that the molecular ratio $SiO_2 : Al_2O_3 = 3 : 1$. Under such conditions, as de Sigmond has shown (*loc. cit.*), almost complete precipitation takes place of the compound $3SiO_2,Al_2O_3,Na_2O,3H_2O$. When the p_H of the mixture was progressively altered by the addition of different

FIG. 4.



Equivalents of sodium taken up, $\times 10^4$.

Full curve: 1/2000 *mol.* (0·17 *g.*) *of synthetic aluminosilicate in* 50 *c.c.*
Dotted curve: 1 *g. of clay No.* 14637; 1% *suspension.*

amounts of standard hydrochloric acid, the amount of sodium retained by the compound varied with the p_H in a manner rather similar to that in the case of clay (Fig. 4). This very highly gelatinous compound was washed several times by decantation after centrifuging, and evaporated to dryness on a water-bath with frequent stirring to cause the formation of small aggregates. It was then dried at 100° and subjected to a process of alternate grinding in a wet condition in an agate mortar and sedimentation. The product was kept for 4 weeks with $N/100$-hydrochloric acid, the acid being renewed at intervals. It was then washed by decantation and centrifuging until it deflocculated and the specific resistance of a 1% suspension was 13,000 ohms. The alternate

grinding and sedimentation was then repeated, but even after this, most of the material sedimented within 3 hours, so that it was still much coarser than clay, which may be stable for months. This material on standing developed an alkaline reaction (p_H 8). The following table compares the imbibitional water and the behaviour towards sodium and calcium hydroxides of this substance with the same properties of different clays and silica as given by Joseph (*J. Agric. Sci.*, 1927, **17**, 14).

Sample No.	Description.	Na taken up in solid phase: 0·5*N*-NaCl+ 0·04*N*-NaOH (1% clay).	Total NaOH neutralised (0·08*N*-NaOH; 1% clay).	Ca removed in solid phase (0·3% clay).	Imbibitional water.
14637	Gezira.	$10·0 \times 10^{-4}$	12×10^{-4}	30×10^{-4}	143
10118	Kaolin.	0·0	0·0	1	5
13107	Mongalla (red).	3·1	19	22	54
—	Bentonite.	7·6	20	36	362
—	Synthetic aluminosilicate.	24	40	51	74
—	Amorphous silica.	4	About 70	About 70	40
10120	Ball clay.	—	—	—	40

The synthetic product is remarkable for its high sodium-absorbing capacity. All the clays neutralise more calcium than sodium hydroxide. This may be connected with the fact mentioned by Vernadsky (*Rep. Brit. Assoc.*, 1923, 435) that it is a general property of zeolites to form additive compounds with calcium hydroxide. The synthetic material shows a marked contrast with kaolin both in its reactions with bases and in its imbibitional water. It retains 13% of moisture at 150°, in this respect also resembling clays. Kaolin has been prepared synthetically by Schwarz and Walcker (*Z. anorg. Chem.*, 1925, **145**, 304) by precipitating silicic acid with aluminium chloride in an *acid* medium.

Although the first-mentioned synthetic aluminosilicate resembled clay in some important respects, yet its physical properties, as exemplified by its plasticity in the hand, showed that this most characteristic property of clay was only present to a very limited extent—possibly this may be due to the coarseness of its particles. Notwithstanding that bentonite is by far the most highly colloidal clay-like substance known, yet it takes up less sodium than the Gezira clay, whilst silica, which has no clay-like properties, takes up more sodium than the Mongalla clay. The sodium absorption of these substances is therefore not necessarily related to their colloidal properties or to the fineness of division of their particles.

Summary.

1. Clay which has been purified after a mild acid treatment takes up equivalent quantities of bases up to a p_H of about 9.

When the p_H is greater than this, the amounts removed are in the order lithium < sodium < potassium < barium < calcium. These amounts are increased by the presence of neutral salts of the metals.

2. The amount of sodium hydroxide neutralised in the form of *soluble* compounds is negligible until the p_H is above 9, but increases rapidly when the alkalinity is greater than this.

3. These results, taken in conjunction with evidence from elsewhere, are accounted for on the supposition that clay is an insoluble or a colloidal weak acid in *direct* equilibrium with bases in solution, the salts formed with the various bases being equally insoluble; but unless the alkali is very dilute ($p_H = 9$), the clay begins to break down, giving silicates and aluminates. With sodium these are easily soluble, and with calcium they are insoluble, whilst barium and potassium occupy intermediate positions.

4. About 1% of the clay was immediately dissolved by $N/10$-sodium hydroxide, but this amount was only slightly increased on prolonged standing. Renewal of the alkali, however, rapidly caused the dissolution of 1% more. The ratio of silica to sesquioxides in solution increased from 1 to 6 in four successive treatments. The imbibitional water of the clay was unaltered by the above treatment.

5. The viscosity and specific volume of coagulated clay show pronounced maxima between p_H 8 and 10 with caustic soda, but not with sodium carbonate at the same p_H values.

6. In base-absorption, water-retention, and imbibitional water a synthetic aluminosilicate showed considerable analogy with clay, although the material was comparatively coarse and was only slightly "clay-like" to the touch. Large sodium absorption by aluminosilicates does not necessarily indicate highly developed colloidal properties or a particularly fine state of division. Comparisons are made between three different clays—kaolin, silica, and bentonite.

WELLCOME TROPICAL RESEARCH LABORATORIES,
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CCCLXXIX.—*On Active Nitrogen. Part IV. The Independence of the Afterglow and the Chemical Properties of Active Nitrogen.*

By ERIC JOHN BAXTER WILLEY.

SINCE the discovery by the present Lord Rayleigh (Strutt, *Proc. Roy. Soc.*, 1911, *A*, **85**, 219) that nitrogen which has been subjected to the action of a condenser discharge at low pressures shows both

an afterglow and chemical activity, there has been much discussion as to whether this active modification of the element is (*a*) atomic, (*b*) molecular and metastable, or (*c*) triatomic. The evidence for each of these views may shortly be summarised :

(*a*) (i) The decay process of the glow follows a bimolecular law (Angerer, *Physikal. Z.*, 1921, **22**, 97).

(ii) An analysis of the banded afterglow spectrum (Birge, *Nature*, 1926, **117**, 80), critical potential measurements in connexion with this (Sponer, *Z. Physik*, 1925, **34**, 622), and observations upon the spectra excited by active nitrogen (Mulliken, *Physical Rev.*, 1924, **23**, 259, 767 ; 1925, **26**, 1) lead to the view that the energy associated with this glowing gas is of the order of 200,000—250,000 cals./g.-mol. (10—12 volts).

(*b*) Saha and Sur (*Phil. Mag.*, 1924, **118**, 421) consider that the spectroscopic evidence indicates a metastable molecule of heat of formation 190,000 cals./g.-mol.

(*c*) Trautz (*Z. Elektrochem.*, 1919, **25**, 299), from mathematical considerations, favours a triatomic molecule with a heat of formation of 5,000—10,000 cals./g.-mol.

The consensus of opinion regards active nitrogen as possessing a *high* heat of formation and its existence as due to atomic recombination, an excited or metastable and chemically reactive molecule thus being produced.

In Parts I, II, and III of this series (J., 1926, 1804 ; this vol., pp. 669, 2188), evidence has been presented for the view that the energy of active nitrogen is 45,000 cals./g.-mol. (2 volts), and deductions from the spectra excited by active nitrogen have been criticised on the ground that chemiluminescence has not been sufficiently considered as a possible means of production of these luminous phenomena (*Nature*, 1926, **118**, 735). Efforts recently made (Ruark, Foote, Rudnick, and Chenault, *J. Opt. Soc. Amer.*, 1927, **14**, 17) to answer these objections are unsatisfactory, since the calculations made here are based upon mercurous azoimide, HgN_3, and not upon the substituted ammonias, Hg_3N_2 and Hg_3N, which are the products of the reaction between active nitrogen and mercury vapour.

Thus we are left to reconcile two entirely different views on the energy and nature of active nitrogen, each supported by abundant experimental evidence, and as a tentative explanation it was suggested (Part II) that active nitrogen might emit its energy in a series of 45,000-cal. (2-volt) stages.

Early in 1925 it had been felt that certain seemingly inconsistent observations upon active nitrogen could best be explained by the theory that *two* luminous forms of the element were concerned,

differing both in chemical activity and in nature, but as this view led to the assumption of a possible change in the spectrum of the glow during decay, owing to the transformation rates of the two species not being the same, the hypothesis was for the time being abandoned. Dr. H. W. B. Skinner has recently suggested to the author that the discrepancy in these two sets of experiments can be overcome if we do not regard the chemically active nitrogen as luminous at all, but ascribe all the luminous phenomena (if this be possible upon the basis of available experimental evidence) to the effects of a few atoms produced at the same time as the former substance. This theory has, it is believed, been completely verified, for it has been found that the destruction of the glow by a second weak discharge and also by heat, noticed by Lord Rayleigh, is not accompanied by any decomposition of the chemically active nitrogen; furthermore, activity can be produced in the gas by the use of a discharge which does not give rise to any glow.

Experimental.

First Method.—Lord Rayleigh has shown (*Proc. Roy. Soc.*, 1916, *A*, 92, 438) that when a stream of glowing nitrogen is drawn through a second and weak discharge, the glow is completely or very largely destroyed, and it appeared possible that this second discharge might prove fatal to the luminous nitrogen without affecting the chemically active modification which is, *ex hypothesi*, also present. This possibility was tested in the following manner.

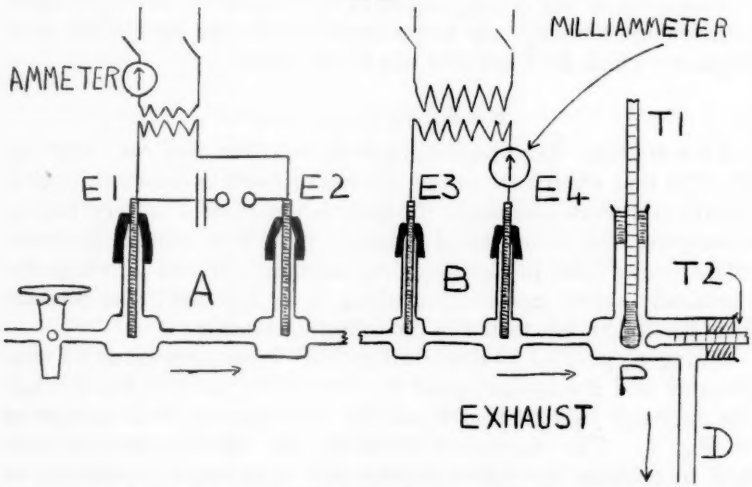
Nitrogen, purified as described in Part I, was drawn at 10 mm. pressure and a constant speed (1—3 litres/hr., at *N.T.P.*) through the discharge tubes A and B and the test chamber P to exhaust at D (Fig. 1). The aluminium electrodes E1, E2, E3, and E4 were held in position by rubber sleeves and their relative positions so adjusted that the distance between E2 and E3 was $1\frac{1}{2}$ times the distance between E3 and E4. Projecting into the test chamber P were two identical and carefully calibrated thermometers, T1 and T2, the bulb of the former being coated with a small and closely adherent piece of oxidised copper gauze, while the latter was bare. It was found in calibration experiments that, when active nitrogen was drawn through the apparatus, the glow was extinguished at the surface of the copper oxide, and that the rise in temperature shown by T1 above that indicated by T2 was strictly proportional to the concentration of active nitrogen at the position of the bulb of T1, this concentration being determined by means of nitric oxide, as described in Part I. This heating effect in T1 is obviously due to the catalytic decay of the active nitrogen at the copper oxide surface (compare Part III), as was proved by warming the tubes A and B

by small flames while a stream of inert nitrogen was drawn through the apparatus; the temperatures recorded on T1 and T2 were then identical.

The difference in temperature between T1 and T2 is thus a measure of the concentration of active nitrogen in the gas. A strong discharge, capable of developing the afterglow, was maintained in A from the coil, condensers, and spark gaps connected as shown, and a weak direct induction coil or transformer discharge from another circuit could, if desired, be run in B.

Lord Rayleigh's observation as to the destruction of the afterglow in these circumstances was confirmed, no luminosity being visible in the gases emerging from B when a weak discharge was maintained

FIG. 1.



between E3 and E4. (Any tendency for the auxiliary discharge to wander and pass between E2 and E3, E2 being connected to earth, was overcome by the electrode-spacing arrangement already mentioned.)

It was found, however, that provided too strong a discharge was not employed in B, the concentration of active nitrogen as measured on T1 and T2 did not change appreciably, in spite of the complete destruction of the glow by the auxiliary discharge; too strong a discharge in B destroyed both the glow and the chemical activity (Table I). The conditions necessary for the retention of the latter were best realised in practice by means of a discharge from a small transformer run off the 100-volt A.C. mains and provided with a series resistance of 825 ohms in the primary; the secondary current was then about 0·1 milliamp. (R.M.S. value) at 500 volts. The same

TABLE I.

No.	No. of observations.	T1.	T2.	T1—T2.	Flow speed of gas at 13 mm. press. (c.c./hr.).	Auxiliary transformer discharge.	Effect on afterglow.	
1	9	1·6°	1·2°	0·4°	—	Coil.	Completely extinguished.	
2	8	1·0	1·0	0·0	—	Weak.	,,	,,
3	15	1·0	1·0	0·0	—	,,	,,	,,
4	11	0·9	0·9	0·0	—	,,	,,	,,
5	17	2·7	1·3	1·4	2800	Medium.	,,	,,
6	8	4·3	0·6	3·7	3000	Strong.	,,	,,
7	10	2·9	0·4	2·5	—	,,	,,	,,
8	10	0·8	0·6	0·2	1900	Weak.	,,	,,
9	12	2·0	0·8	1·2	2000	,,	,,	,,
10	12	2·1	0·7	1·4	,,	Medium.	,,	,,
11	12	2·1	0·6	1·5	,,	,,	,,	,,

effect could be produced by the use of a direct coil discharge in B, but on account of the difficulty in regulation, the transformer was more generally used.

Furthermore, whilst in some cases a decrease in the concentration of active nitrogen was noticed, this was by no means comparable with the complete or almost complete destruction of the afterglow, and hence it appears that there is no simple relation between the intensity of the afterglow and the amount of chemically active nitrogen present.

Second Method.—In view of the comparatively insensitive nature of this device for detecting and determining the active nitrogen, the experiments were repeated, the estimations being carried out with nitric oxide; the other experimental arrangements remained unaltered. The technique of this method has been considerably improved and a short account of it may be given.

The nitrogen from the discharge tube B entered the reaction chamber at E (Fig. 2), and at N an inlet was provided for the nitric oxide, regulation of this gas being effected by means of the capillary choke at C and the tap S5. (The nitric oxide was prepared by dropping a solution of sodium nitrite into an acidified solution of ferrous sulphate, and was dried by phosphorus pentoxide.) The gases then passed to exhaust *via* the two-way tap S1, the condensing trap R1, and the second two-way tap S2. The system S3, R2, and S4 was identical with and parallel to the circuit just described. One side of S1 and S3 was connected to a supply of pure, dry hydrogen, and S2 and S4 were connected to exhaust and also to a train of absorption bulbs for the determination of the nitrogen peroxide. Hence, by the use of these two condensing systems, continuous estimations of the concentration of active nitrogen can be made without stopping the apparatus; the nitrogen peroxide

produced by the action of the active nitrogen upon nitric oxide condenses in R1 (or R2), which is cooled by liquid air. At the end of the experiment the gas stream is diverted to the other condensing system, the contents of R1 are allowed to warm to room temperature, and then blown by means of hydrogen (admitted at S1) through a train of absorption bottles containing a 10% solution of potassium iodide, the current of gas being maintained for some 20 minutes in order to clear the last traces of nitric oxide from the solution; the iodine is then titrated by means of standard sodium thiosulphate solution and the concentration of active nitrogen

FIG. 2.

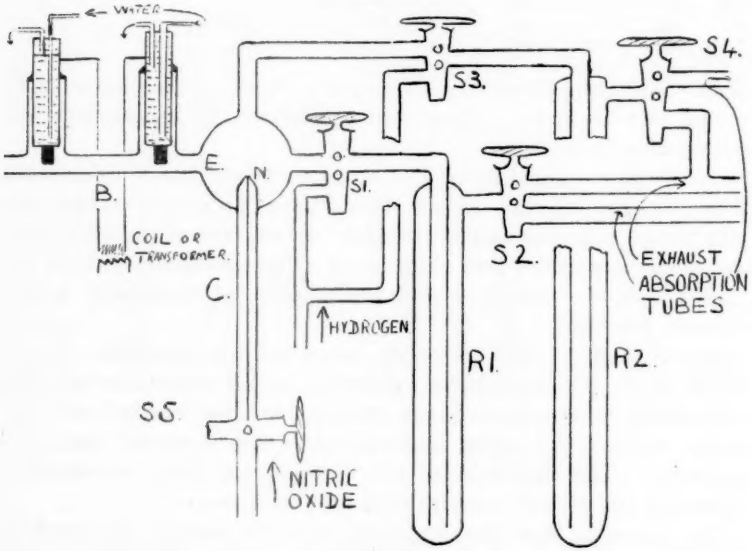


TABLE II.

Series.	No. of expts.	% Active nitrogen. (1) main discharge.	% Active nitrogen. (2) main + auxiliary discharge.	Difference (2) − (1).	Auxiliary transformer discharge.
1	5	0·90	1·20	0·30	Weak.
2	4	2·30	2·50	0·20	,,
3	4	1·70	1·70	0·00	,,
4	4	1·75	2·00	0·25	,,
5	5	1·40	1·30	−0·10	Strong.
6	7	1·85	1·75	−0·10	,,
7	5	1·15	1·30	0·15	Weak.
8	8	1·30	1·30	0·00	,,

calculated as already described (Part I). The results of these experiments are given in Table II, and it will be noticed that, whilst in some cases the concentration of active nitrogen has diminished,

yet in other cases it has increased when the second discharge is employed. Since in every case the destruction of the glow is complete in the gases issuing from the auxiliary discharge, it appears that the results already obtained are confirmed, and that it is possible by this method to destroy the glow and yet retain the chemical properties of active nitrogen.

Third Method.—It was felt that these observations could be made still more convincing if a stream of non-luminous but chemically active nitrogen could be obtained by a single operation, and in view of the known production of active nitrogen in the arc, where none of the luminous phenomena connected with active nitrogen are to be seen (Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 260), it was decided to study the effect of the uncondensed discharge upon nitrogen.

For this purpose, the apparatus employed was as in Fig. 2, except that the tubes A and B were replaced by another discharge tube with water-cooled Armco electrodes. The discharge was obtained from a rotary converter and transformers and took 10—20 milliamps. at 2000—3000 volts; in these circumstances, the emergent gases showed no perceptible luminosity but contained a considerable quantity of active nitrogen (Table III). No traces appeared here

TABLE III.

Series	1	2	3	4	5	6	7
No. of expts.	6	6	4	6	5	3	5
% Active nitrogen	0·84	0·98	1·28	0·64	0·85	1·52	1·52

of the green flame usually to be seen where nitric oxide enters a stream of glowing nitrogen, and hence we must conclude that most probably this particular development of luminosity is independent of the actual chemical reaction in progress (compare Lord Rayleigh, *Proc. Roy. Soc.*, 1911, *A*, **86**, 56). Furthermore, strong indications of the presence of active nitrogen were obtained by the use of the two-thermometer device already described.

Fourth Method.—The methods of extinguishing the luminosity of the active nitrogen have hitherto been electrical in nature, and it is obviously of importance that other means should be attempted in order that a satisfactory mechanism may be formulated for the glow-destruction process. Lord Rayleigh has shown (*Proc. Roy. Soc.*, 1911, *A*, **85**, 219) that, when a stream of glowing nitrogen is drawn through a tube which is heated, the luminosity ceases at the hot portions and reappears in the colder parts if the temperature is not too high; if the tube be heated too strongly, however, the glow is not restored at all, and it was thought advisable to study this phenomenon in the light of the present observations.

The apparatus employed is as in Fig. 2, except that the auxiliary discharge tube was replaced by a U-tube of some 10″ over-all length and ¼″ internal diameter; determination of the active nitrogen was made with nitric oxide as before. The U-tube was immersed in an electrically heated bath of heavy paraffin; for temperatures above 250° the paraffin was replaced by a mixture of sodium and potassium nitrates.

When a stream of glowing nitrogen was drawn through the apparatus at a rate of 2000 c.c./hr. and 10 mm. pressure, the luminosity was considerably enhanced as the temperature of the bath was raised from 20° to 80°; from this point to about 225° no appreciable change in intensity was noticed, but at 235° the luminosity began to decrease in the gas entering the detection chamber, at 250° the effect was pronounced, and at 300—320° the gas lost all glow. Contrary to the observations of Lord Rayleigh, the glow did not as a rule reappear beyond the hot zone when once it had been destroyed, although a 2-litre chamber was provided in the exhaust line in order that this point might be examined; in some cases, however, his observations were confirmed, and it appears that the nature of the hot surface is a very important factor in this connexion.

TABLE IV.

Series.	No. of expts.	Temp. of bath.	Glow.	% Active nitrogen.
1	2	15°	Strong.	0·64
	2	80	Slightly enhanced.	0·73
	1	139	,, ,,	0·64
	1	257	,, ,,	0·66
	1	252	,, ,,	0·69
2	3	15	Strong.	0·71
	3	330	Practically extinguished.	0·71

Determinations of the active nitrogen in these experiments showed (Table IV) that, in spite of the alterations in the degree of luminosity, the concentration of the active gas remained sensibly unchanged throughout.

Discussion.

The experiments just described provide, it is thought, not only a fairly complete solution to the difficulty in reconciling spectroscopic and other optical work upon active nitrogen with the observations made upon the same subject in this laboratory, but also an explanation of certain phenomena alluded to by Lord Rayleigh and others.

Just before these experiments were completed, Bonhoeffer and Kaminsky (*Z. Elektrochem.*, 1926, **32**, 536) showed that the concentration of active nitrogen (measured chemically) and the intensity of the glow are not simply related to one another, at least four

terms being necessary in any expression connecting these two quantities. Details of their experimental procedure are not available, but the present work is in complete agreement with theirs. It may also be noticed that Koenig and Elöd (*Ber.*, 1914, **47**, 516) suspected that the presence of a glow was not a necessary criterion of chemical activity in nitrogen, but here again no experimental evidence was adduced. Furthermore, Lord Rayleigh has stated that "there does not appear to be any close or necessary connexion between the luminous phenomena associated with active nitrogen and the chemical ones" (J., 1918, **113**, 200; see also *Proc. Roy. Soc.*, 1913, *A*, **88**, 539). It appears that we must decide between two theories for an explanation of these phenomena :

(i) Active nitrogen may be regarded as a homogeneous substance which emits its energy in two or more stages, one of these being invariable and giving rise to the chemical activity, and the other or others being capable of modification so that the residual energy may be lost either as ultra-violet radiation or by an increase in the kinetic energy of the molecule. Saha and Sur (*loc. cit.*) regard the visible or α-radiation of the afterglow as *secondary* (the primary band in nitrogen lying in the vicinity of $\lambda = 1400$ Å.U.); it is possible therefore that some influence might lead to suppression of these α-bands and a corresponding development of other parts of the spectrum without affecting the chemical activity.

(ii) The whole of the observations and measurements which have been made with regard to active nitrogen can, in the author's opinion, be much more readily explained if it is assumed that the luminous and chemically active forms are quite distinct, although usually coexistent. The multiplicity of ionised and excited bodies produced by the discharge in any gas renders this quite likely, and examples are known of the formation under these conditions of more than one active form of an element, *e.g.*, the active oxygen, distinct from ozone, of Koenig and Elöd (*loc. cit.*), and the mono-, di-, and tri-atomic forms of hydrogen, all chemically active, whose existence has been claimed severally by Bonhoeffer (*Z. physikal. Chem.*, 1924, **113**, 199; 1925, **116**, 114, 391; 1926, **119**, 474; *Z. Elektrochem.*, 1925, **31**, 521), Phipps and Taylor (*Physical Rev.*, 1927, **29**, 309), and Wendt and Landauer (*J. Amer. Chem. Soc.*, 1922, **44**, 510).*

* It may be suggested that differences in the reactions of active hydrogen reported by certain of these investigators, *e.g.*, the formation of ammonia with nitrogen, noticed by Wendt and Landauer (*loc. cit.*) and denied by Bonhoeffer (*loc. cit.*; see also Paneth, Klener, and Peters, *Z. Elektrochem.*, 1927, **33**, 102), may be due to differences in their experimental conditions leading to the formation of different substances : the chemical activity of H, H_2, and H_3 is not likely to be the same.

If this view is adopted, it is apparent that the difficulties discussed earlier are overcome, since the observations of an active nitrogen made by spectroscopists and by workers in this laboratory have really been upon different modifications of the same element. The author now suggests that active nitrogen consists of a mixture of (i) metastable molecules with a heat of formation of *ca.* 45,000 cals./g.-mol. (2 volts), which are exclusively responsible for the chemical activity, and (ii) a much smaller proportion (probably of the order of 10^{-7}) of atoms which upon recombination produce high-level excited molecules, the energy set free, equivalent to 200,000—250,000 cals./g.-mol. (10—12 volts) being liberated as radiation; all the luminous phenomena and excitation of spectra, with the possible exception of certain cases of chemiluminescence arising from reactions of the 2-volt metastable molecules, are to be ascribed to this second constituent.

The decay of the afterglow follows a process which is bimolecular only with respect to the atoms, but is in reality a ternary reaction, for it has been shown (Herzfeld, *Z. Physik*, 1922, **8**, 132; Polyani, *ibid.*, 1920, **1**, 337; Born and Franck, *Ann. Physik*, 1925, **76**, 255) that, when two atoms recombine to form a diatomic molecule, the presence of a third body is nearly always necessary in order that considerations of the conservation of energy and momentum shall be satisfied. Such a view would presuppose a relation between the total pressure of the gas and the rate of decay of the afterglow; this has actually been observed by Lord Rayleigh (*Proc. Roy. Soc.*, 1916, *A*, **92**, 438) and studied by the present author, and it is hoped to publish details in a later communication.

The action of traces of impurities in developing the afterglow would appear to be adequately accounted for by Lord Rayleigh's original explanation (*Proc. Roy. Soc.*, 1912, *A*, **86**, 262; **87**, 179). Its behaviour towards heat and cold will be discussed in a later communication.

The catalytic destruction of the glow by surfaces, and by copper and other metals in particular, may readily be explained by the well-known analogous case of the surface recombination of hydrogen atoms. The extinction of the luminosity when a metal surface begins to be active in promoting the decay of the *chemically* active nitrogen is also accounted for when we remember that the surface is, *ex hypothesi*, composed of the metal, and not of the nitride, when the point of activity is reached; there is no apparent reason why a nitride surface should catalyse the recombination of nitrogen atoms, but the parent metal itself may, from the analogy already mentioned, be very effective in this connexion. It follows that the action of the discharge in extinguishing the luminosity is not intrinsically

electrical, but that the bombardment of the glass of the discharge tube by the ions and electrons present simply leads to the production of a " clean " surface, upon which the recombination of atoms can take place with ease; heat also leads to the production of this very active surface. The production of a few ions during the decay of the afterglow in phenomena studied by Constantinides (*Physical Rev.*, 1927, **30**, 95) is probably due to a side reaction among the atoms undergoing recombination on the surface.

It is clear that the relationship between concentration of active nitrogen, C, and glow intensity, I, as well as the magnitude and sign of dI/dC at any instant, will vary with the nature and area of the surfaces present. It appears probable that the mechanism whereby the chemically active nitrogen is destroyed in the discharge is analogous to that of the electrical production of ozone, and that the same complicated mixture of electrical and surface factors is involved : much more experimental evidence is needed upon this point.

It remains to discuss the probable nature of the chemically active modification of nitrogen. If this were triatomic, it would be expected that such a large molecule should condense easily (see Lord Rayleigh, *Proc. Roy. Soc.*, 1911, *A*, **86**, 56), and the author is indebted to Sir J. J. Thomson for the information that evidence is not lacking that such a separation can be effected under appropriate conditions.

The present author suggests, however, that the most cogent evidence as to the nature of active nitrogen is provided by the compounds it produces in its chemical reactions. With the metals, compounds are produced which, as a rule, give quantitative yields of ammonia when hydrolysed, *e.g.*, magnesium nitride; pentane gives hydrogen cyanide, amylenes, and ammonia (Koenig and Elöd, *loc. cit.*); and in general *when active nitrogen reacts with other substances it gives rise to derivatives of ammonia and not to substituted azoimides, hydrazines, etc.* These substances are invariably of the type produced in the few reactions of *inert* nitrogen, and hence the presumption is that active and ordinary nitrogen cannot be very different in structure. It is clear that if active nitrogen were atomic in character we should have to postulate dissociation of the molecule as an invariable prelude to the reactions of *inert* nitrogen, which does not appear likely. May it not be that the active modification is simply an isomeride of nitrogen, such as an acetylenic molecule ? By analogy with its family congeners of the Periodic Table, nitrogen might be expected to exhibit allotropy, but much more experimental evidence is necessary before any conclusions can be reached upon this point.

Summary.

Four series of experiments are described in which it is shown that nitrogen can be chemically active and yet show no visible luminosity whatever. These are believed to indicate that "active" nitrogen consists of a mixture of a non-luminous, chemically active substance together with a very small proportion of atoms, the latter being responsible, upon a termolecular recombination, for the afterglow and the greater part of the excitation of spectra observed when various substances are admitted to the glowing gas. The heats of formation of the two varieties, the former of which is regarded as being most probably a metastable diatomic or an acetylenic molecule, are respectively about 45,000 and 200,000—250,000 cals./g.-mol.

This explanation is thought to reconcile the chemical and spectroscopic views, and also accounts for the whole of the phenomena connected with active nitrogen.

The author's thanks are due to the Department of Scientific and Industrial Research for a grant which enabled the converter and transformers to be purchased; to Dr. E. K. Rideal for his continued interest in these researches; to Mr. R. E. D. Clark, who has proved a capable assistant in some of the experimental work; and above all to Dr. H. W. B. Skinner, to whom this particular investigation must be dedicated.

Addendum.—Since the above was written, Crew and Hulbert (*Physical Rev.*, 1927, **30**, 124) have described some experiments on the dissociation of gases in the discharge at low pressures (5 mm. and less). The extent of dissociation is about 100% for wet hydrogen, rather less for the dry gas, 60% for oxygen, but close to zero for nitrogen, carbon monoxide, and carbon dioxide under the same conditions; the results with uncondensed and with condensed discharges, the latter producing the afterglow in nitrogen, are almost identical. This would appear to show once again that the chemically active nitrogen (which is produced to the extent of at least 5% under these conditions) cannot be atomic in character, and the work confirms the author's view upon this subject.

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CAMBRIDGE. [*Received, September 6th*, 1927.]

CCCLXXX.—*Molecular Structure in Solution. Part III. The Electrical Conductivities of Aqueous Solutions of Cobalt Chloride and Hydrochloric Acid, with a Note on the Prediction of Crystal Structure.*

By Owen Rhys Howell.

The densities, viscosities, refractive indices, and surface tensions of a series of solutions containing a constant amount of cobalt chloride with increasing amounts of hydrochloric acid, and the same properties of an exactly similar series of solutions of hydrochloric acid alone have already been determined (this vol., pp. 158, 2039). The differences in the values of each of these properties for corresponding members of the two series throw light upon the change in the state of the cobalt atom in solution with increasing acid concentration. All the results obtained have been fully interpreted by assuming that, in accordance with the theory of the colour of the cobaltous compounds suggested by Hill and Howell (*Phil. Mag.*, 1924, **48**, 833), the cobalt atom is forced out of its association with 6 molecules of water into one with 4 atoms of chlorine.

The electrical conductivities of these solutions have now been examined, and the conclusions drawn from the results are in complete accord with those already indicated.

Experimental.

Determination of Electrical Conductivity.—The electrical conductivities were determined in the usual way by the use of a standard resistance, an alternating current from a small coil, a metre bridge, and a low-resistance telephone. A small U-shaped cell made of resistance glass and having a capacity of about 3 c.c. was employed. It was immersed to below the level of the solution in a thermostat at 20° ± 0·02°. With each solution at least three different known resistances were employed and the point of balance was determined at least four times for each. With each known resistance the mean point of balance was taken and the conductance of the cell calculated. In almost every instance, the values lay within 0·05% of the mean, and in no case did the difference exceed 0·1%.

The cell constant was determined with *N*-potassium chloride solution, prepared from the pure salt (Kahlbaum's), which was first recrystallised and dried. The conductivity of this solution at 20° is 0·10207 mho (Kohlrausch, Holborn, and Diesselhorst, *Wied. Ann.*, 1898, **64**, 417); the actual resistance was found to be 3028

ohms, whence the conductance was 0·0003302 mho and the cell constant 309·1.

Materials.—The solutions used for these determinations were the same as those employed for the measurement of the refractive index and surface tension (*loc. cit.*). A few new solutions were also prepared from the same stock solutions as those previously employed. The water used for preparing these solutions was twice redistilled; its conductivity was negligible compared with that of any of the solutions.

Results.

Conductivities.—The conductivities of the series of solutions of hydrochloric acid alone are given in column 3 of Table I. Previous measurements for concentrated solutions of hydrochloric acid have been made at 18° by Kohlrausch (*Pogg. Ann.*, 1876, **159**, 233) and at 25° by Masson and Green (J., 1908, **93**, 2023). Direct comparison with these is not possible because of the different temperatures employed, but the curve of the values now given lies smoothly between those of the other observers. The values of the conductivity are plotted against the normality of the acid (at 18°) in Fig. 1 (upper curve).

TABLE I.

Electrical Conductivities.

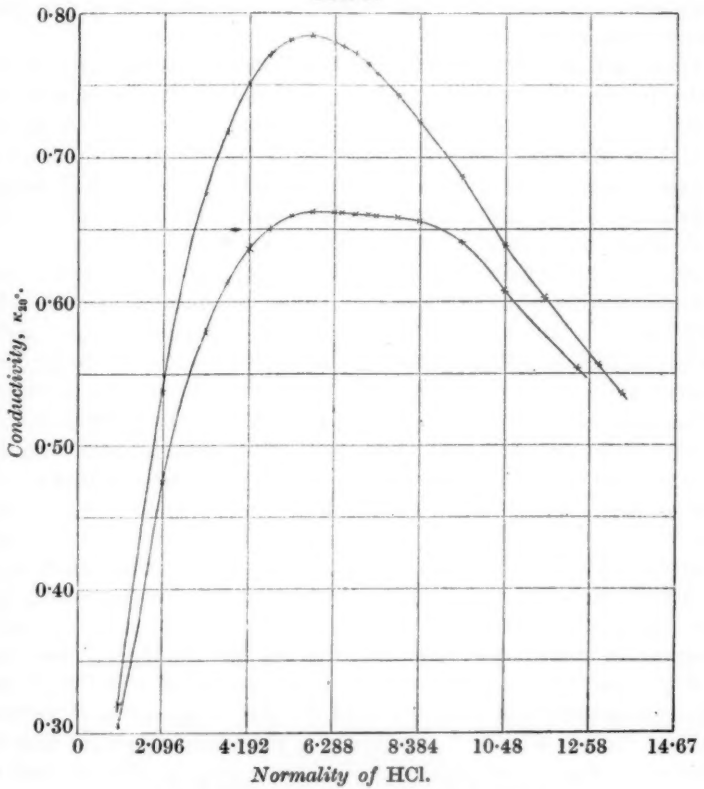
1. Normality of HCl, $N_{18°}$.	2. Conductivity of $CoCl_2$+HCl, $\kappa_{20°}$.	3. Conductivity of HCl alone, $\kappa_{20°}$.	4. Diff., 2—3.	1. Normality of HCl, $N_{18°}$.	2. Conductivity of $CoCl_2$+HCl, $\kappa_{20°}$.	3. Conductivity of HCl alone, $\kappa_{20°}$.	4. Diff., 2—3.
0	0·06358	—	+0·0636	6·812	0·6611	0·7728	−0·1117
1·048	0·3053	0·3196	−0·0143	7·126	0·6605	0·7647	−0·1042
2·096	0·4742	0·5375	−0·0633	7·336	0·6599	0·7585	−0·0986
3·144	0·5797	0·6760	−0·0963	7·860	0·6584	0·7434	−0·0850
3·668	0·6132	0·7190	−0·1058	8·384	0·6556	0·7258	−0·0702
4·192	0·6361	0·7508	−0·1147	9·432	0·6408	0·6874	−0·0466
4·716	0·6503	0·7715	−0·1212	10·48	0·6068	0·6389	−0·0321
5·240	0·6599	0·7823	−0·1224	11·48	—	0·6021	—
5·764	0·6624	0·7854	−0·1230	12·26	0·5530	0·5749	−0·0219
6·288	0·6624	0·7799	−0·1175	12·83	—	0·5564	—
6·498	0·6618	0·7771	−0·1153	13·38	—	0·5357	—

The results obtained with the series of solutions of cobalt chloride and hydrochloric acid are given in column 2 of Table I, and plotted against the normality of the acid in Fig. 1 (lower curve). The two curves are very different in form: that for the acid only rises to a sharp maximum, whereas that for the solutions containing cobalt is greatly flattened at its maximum.

The differences in conductivity between corresponding solutions in the two series are given in col. 4 of Table I and are plotted against

the normality of the acid in Fig. 2. It is seen that the conductivity-differences curve is almost the exact complement of the viscosity-differences curve, which is also reproduced for comparison; the minimum of the one occurs at the same concentration of acid as the maximum of the other. There is one point of difference, *viz.*, that whereas the viscosity-differences curve first falls slightly

FIG. 1.



Upper curve: Solutions of hydrochloric acid only.
Lower curve: Solutions of hydrochloric acid + cobalt chloride.

before rising to its maximum, the conductivity-differences curve falls continuously to its minimum. The same reasoning which accounted for the form of the first (this vol., p. 168) also explains that of the second, including this respect in which they differ.

The effect of increasing the concentration of acid is to throw more and more of the cobalt out of its association with 6 molecules of water, $Co(H_2O)_6^{\cdot\cdot}$, into one with 4 atoms of chlorine, $CoCl_4''$. When this transition is complete, continued increase in the con-

centration of acid would be without further effect, and the difference in physical properties between the solutions containing cobalt and the corresponding solutions of acid alone should become and remain constant. It is seen that the conductivity-differences curve, like the viscosity-differences curve, flattens out at the highest concentrations of acid to become parallel to the axis of concentration, indicating that this transition is practically complete. Moreover, both curves exhibit this characteristic at approximately the same concentration of acid.

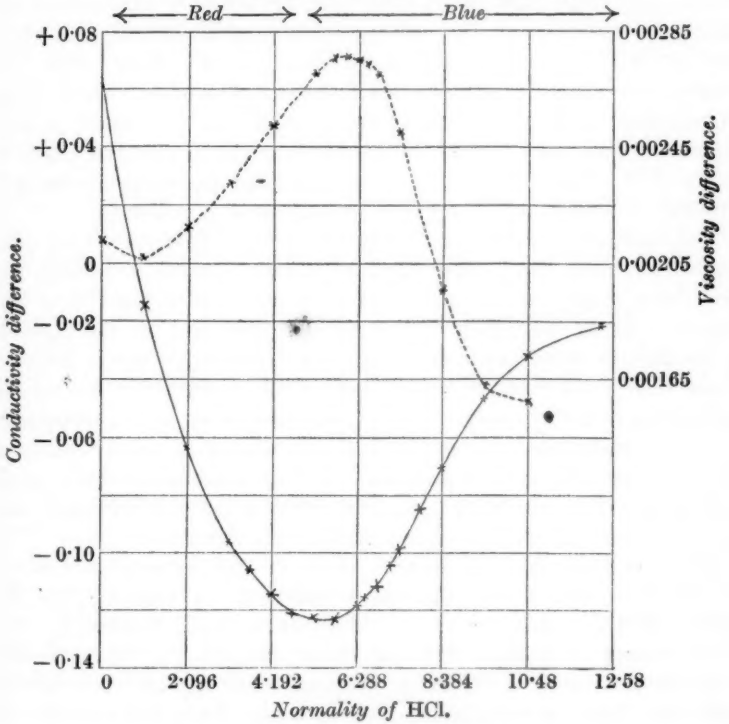
It is seen that the conductivity differences at the end of the series (blue solutions) are smaller than those at the beginning (red solutions). The curve does not, however, fall evenly from the initial to the final value, but exhibits a very deep minimum, just as the viscosity-differences curve similarly shows a well-defined maximum. Since the red and the blue ions, $Co(H_2O)_6^{\cdot\cdot}$ and $CoCl_4''$, are oppositely charged, there will undoubtedly be combination between them where they are present together in solution; they will not remain wholly as free ions. The combination of these ions will result in further dissociation of the compounds from which they are derived, thus liberating chlorine ions and hydrogen ions respectively. These, however, will not remain free, the ionisation being depressed by the hydrochloric acid already present in high concentration, so that the conductivity of the solution will diminish. The greater the combination, the less will be the conductivity of the solution; therefore, as transformation of the red $Co(H_2O)_6^{\cdot\cdot}$ into the blue $CoCl_4''$ proceeds, the conductivity-differences curve falls sharply. The combination will evidently be greatest when these two oppositely charged ions are present in equal amounts, so that the conductivity differences should decrease up to this point. Thereafter, continued transformation of the $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions will result in an increasing surplus of free $CoCl_4''$ and the conductivity differences should increase again up to a constant value. This is seen to be so and it is therefore suggested that the minimum of the conductivity-differences curve occurs when half the cobalt is present as $Co(H_2O)_6^{\cdot\cdot}$ and half as $CoCl_4''$.

The viscosity-differences curve exhibits an initial decrease before rising to its maximum, whereas the conductivity-differences curve falls sharply to its minimum. When discussing the viscosity-differences curve (*loc. cit.*), it was pointed out that the first effect of the addition of hydrochloric acid is to depress the ionisation of the cobalt chloride because of the addition of a common ion. There is thus at first a decrease in the number of the viscous $Co(H_2O)_6^{\cdot\cdot}$ ions, resulting in a decrease of viscosity. This effect is soon overwhelmed by the conversion of $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions,

so that the curve exhibits only a small dip and then rises rapidly. The two effects are thus opposed when the viscosity of the solutions is concerned; but they operate together when the conductivity is considered. Both the initial depression of ionisation and (as discussed above) the conversion of $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4^{\prime\prime}$ ions result in a decrease of conductivity, so that the conductivity-differences curve falls continuously to its minimum.

FIG. 2.

Colour of the cobalt solution in transmitted light.



Full curve: Conductivity differences.
Broken curve: Viscosity differences.

It may readily be shown that the curve of the differences of specific resistance is quite different in form from that of the differences of specific conductance. It is very similar to the density-differences and refractive-index-differences curves found previously (*loc. cit.*), in that it exhibits a point of inflexion at the same concentration of acid and then falls, eventually becoming parallel to the axis of concentration, just as these do, and at about the same concentration of acid. It differs from them in first rising to a

maximum, whereas they fall continuously from the beginning; and this difference is explained in exactly the same way as that between the conductivity-differences and viscosity-differences curves.

Note on the Prediction of Crystal Structure.

When the metallic atom of a colourless insoluble compound is replaced, wholly or partly, by cobalt, a pigment is obtained which may be either blue or red, and it has been shown (Hill and Howell, *loc. cit.*), by carrying out this replacement in compounds of known crystal structure, that when the metallic atom is surrounded by *four* other atoms or groups, the resulting pigment is *blue*, and when surrounded by *six*, the pigment obtained is *red*. Thus, when the magnesium atom in spinelle (magnesium aluminate, where it is surrounded by four oxygen atoms) is replaced by cobalt, a blue pigment (cobalt blue) is obtained, but when the magnesium atom in magnesium oxide (where it is surrounded by six oxygen atoms) is similarly replaced, a red pigment (cobalt pink) is produced.

For comparison of their absorption spectra, pigments were prepared, not only from compounds of known crystal structure, but also from a number the structure of which was at that time unknown. From the colour of the pigment obtained, it was possible to predict the structure of the compound from which it was derived. Since that work was published, two of the compounds have been submitted to *X*-ray analysis by different observers, and the structure is in both instances in accord with that predicted from the colour of the corresponding cobalt pigment. The structures of cobalt oxide and cobalt fluoride have also been subsequently determined and are in agreement with the predictions from the theory.

Zinc orthosilicate. If the zinc atom in zinc orthosilicate is replaced by cobalt, a *blue* pigment is obtained. It follows from the theory that in the pigment the cobalt atom is surrounded by *four* other atoms or groups, and therefore that the zinc atom in the original compound is similarly situated. The crystal structure of willemite (zinc orthosilicate) has recently been determined by Zachariasen (*Norsk. Geol. Tidsskr.*, 1926, **9**, 65), who showed it to be isomorphous with phenacite (beryllium orthosilicate), the crystal structure of which was elucidated by W. L. Bragg (*Proc. Roy. Soc.*, 1927, *A*, **113**, 642), who established that the beryllium atom is between four oxygen atoms. It follows that in zinc orthosilicate the zinc atom is similarly placed, as predicted from the theory.

Magnesium orthosilicate. If the magnesium atom in magnesium orthosilicate is replaced by cobalt, a *red* pigment is produced, so that, according to the theory, the magnesium atom in this compound is surrounded by *six* other atoms. This prediction has been verified

by the work of W. L. Bragg and Brown (*Z. Krist.*, 1926, **63**, 538) on olivine (magnesium orthosilicate).

Cobalt oxide. It is well known that when cobalt oxide is melted in the electric furnace, it crystallises in rose-coloured needles (Moissan, *Compt. rend.*, 1892, **115**, 1034; *Bull. Soc. chim.*, 1893, **9**, 955; *Ann. Chim. Phys.*, 1895, **4**, 136). Although the crystal structure of the compound was unknown, the theory enabled us to predict that, since the compound was of the *red* form, the cobalt atom should be surrounded by *six* oxygen atoms, and verification was forthcoming in the work of Goldschmidt, Barth, and Lunde (*Skrifter Norske Videnskaps Akad.*, No. 7, 1925), of Natta and Reina (*Atti R. Accad. Lincei*, 1926, **4**, 48), and of Bravo (*Anal. Fís. Quím.*, 1926, **24**, 611), who found that the compound possesses the rock-salt structure, *i.e.*, the cobalt atom is between six oxygen atoms.

Cobalt fluoride. Since anhydrous cobaltous fluoride is *red* (Poulenc, *Compt. rend.*, 1892, **114**, 1426), it could be predicted that the cobalt atom should lie between *six* fluorine atoms. Actually, it has been found (Ferrari, *Atti R. Accad. Lincei*, 1926, **3**, 324) to have the same crystal structure as rutile, in which the titanium atom is surrounded by six oxygen atoms (Vegard, *Phil. Mag.*, 1916, **32**, 65, 505; 1917, **33**, 395; 1926, **1**, 1151; Williams, *Proc. Roy. Soc.*, 1917, **93**, 418; Greenwood, *Phil. Mag.*, 1924, **48**, 654).

Summary.

1. The electrical conductivities of a series of solutions containing a constant amount of cobalt chloride and increasing amounts of hydrochloric acid have been determined.

2. The same properties of an exactly similar series containing hydrochloric acid only have also been determined.

3. The curve of the differences of conductivity of corresponding solutions plotted against the concentration of acid is almost the exact complement of the viscosity-differences curve found in a previous investigation. It exhibits a minimum at the same concentration of acid where the other curve exhibits a maximum. It differs in falling constantly to the minimum, whereas the viscosity-differences curve first falls slightly before rising to its maximum. Both its resemblance to and difference from the viscosity-differences curve are fully explained on the same reasoning as that employed in previous investigations.

4. It is noted that the crystal structure of compounds which yield pigments when the metallic atom is replaced by cobalt can be predicted from the colour of the pigment so obtained. The structures of two compounds (zinc and magnesium orthosilicates) have been determined since the theory of the colour of the cobaltous

compounds was suggested, and they verify the predictions made from the theory. The structures of cobalt oxide and cobalt fluoride are similarly in accordance with prediction from the theory.

The author would again express his thanks to Prof. F. L. Pyman, F.R.S., for giving him every facility for doing this work.

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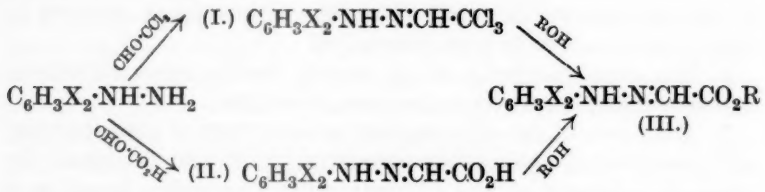
CCCLXXXI.—*The Interaction of Chloral and Arylhydrazines.*

By FREDERICK DANIEL CHATTAWAY and RANDLE BENNETT.

OWING to the violence with which the hydrazone initially formed decomposes, the behaviour of chloral with phenylhydrazine has been little studied. When, however, a 2 : 4-dihalogen-substituted phenylhydrazine is used, the decomposition occurs more quietly and the final products can be isolated. These differ according to the nature of the solvent in which interaction occurs. When any alcohol is used as the solvent, the 2 : 4-dihalogen-substituted phenylhydrazone of the corresponding alkyl glyoxylate (III) is produced identical with the ester yielded by the corresponding dihalogen-substituted phenylhydrazone of glyoxylic acid :



Bromal behaves in an exactly similar manner, although the reaction is not so vigorous as when chloral is used.

When, on the other hand, interaction takes place in water or acetic acid, one molecule of water and one molecule of hydrogen chloride are eliminated and beautifully crystalline, brilliant red compounds formed. When strongly reduced, these yield 2 : 4-dihalogen-substituted aniline; the chlorine atom lost in the decomposition must therefore be one of those contained in the chloral. They are unaffected by heating with acetic anhydride, whilst their intense red colour recalls that of compounds containing an azo-group. Bromine replaces one hydrogen atom not in the nucleus, the substitution product still retaining its red colour.

These red compounds therefore appear to be αα-dichloro-β-2 : 4-dihalogenobenzeneazoethylenes (IV), and the bromine substitution products αα-dichloro-β-bromo-β-2 : 4-dihalogenobenzeneazoethylenes (V), formed thus :

(I.) ⟶ (IV.) $C_6H_3X_2{\cdot}N{:}N{\cdot}CH{:}CCl_2$ ⟶ (V.) $C_6H_3X_2{\cdot}N{:}N{\cdot}CBr{:}CCl_2$.

When the azoethylenes are heated with alcohols they are converted into the corresponding alkyl glyoxylate arylhydrazones (III), but the reaction is not so rapid as that by which the latter compounds are formed from the chloral hydrazones.

Experimental.

Action of 2 : 4-*Dichlorophenylhydrazine Hydrochloride on Chloral Hydrate dissolved in Ethyl Alcohol.*—When 21·5 g. of 2 : 4-dichlorophenylhydrazine hydrochloride (1 mol.) and 16·5 g. of chloral hydrate (1 mol.) were added to 100 c.c. of ethyl alcohol, the liquid became yellow, but little action appeared to take place at the ordinary temperature. On heating, the colour deepened to dark orange and at about 60° hydrogen chloride was evolved, much heat liberated, and the liquid boiled spontaneously for several minutes. The bulk of the alcohol was then slowly distilled off; the residual clear deep yellow liquid, on cooling, deposited bright yellow crystals of *ethyl glyoxylate* 2 : 4-*dichlorophenylhydrazone*, the yield being practically theoretical. This substance is easily soluble in warm alcohol and separates in pale yellow, very slender prisms, m. p. 121·5° (Found : C, 45·8; H, 3·8; N, 11·1; Cl, 27·2. $C_{10}H_{10}O_2N_2Cl_2$ requires C, 46·0; H, 3·8; N, 10·8; Cl, 27·2%). It yielded ethyl alcohol and glyoxylic acid 2 : 4-dichlorophenylhydrazone on hydrolysis, and 2 : 4-dichloroaniline on reduction.

Methyl glyoxylate 2 : 4-*dichlorophenylhydrazone* crystallises in pale yellow, slender prisms, m. p. 136·5° (Found : C, 43·9; H, 3·4; Cl, 28·8. $C_9H_8O_2N_2Cl_2$ requires C, 43·7; H, 3·2; Cl, 29·0%), n-*propyl glyoxylate* 2 : 4-*dichlorophenylhydrazone* in short, pale yellow, flattened prisms, m. p. 65° (Found : Cl, 25·6. $C_{11}H_{12}O_2N_2Cl_2$ requires Cl, 25·8%), and n-*butyl glyoxylate* 2 : 4-*dichlorophenylhydrazone* in slender, yellow, flattened prisms, m. p. 59° (Found : Cl, 24·3. $C_{12}H_{14}O_2N_2Cl_2$ requires Cl, 24·5%).

Action of 2 : 4-*Dibromophenylhydrazine Hydrochloride on Chloral Hydrate dissolved in Methyl Alcohol.*—2 : 4-Dibromophenylhydrazine hydrochloride (15 g.; 1 mol.), chloral hydrate (8 g.; 1 mol.), and methyl alcohol (60 c.c.), when heated together under reflux on a water-bath for an hour, reacted vigorously with liberation of hydrogen chloride. A deep yellow liquid was obtained, from which *methyl glyoxylate* 2 : 4-*dibromophenylhydrazone* separated on cooling.

It crystallises from boiling methyl alcohol, in which it is moderately easily soluble, in slender, pale yellow, flattened prisms, m. p. 136° (Found: C, 32·2; H, 2·5; Br, 47·6. $C_9H_8O_2N_2Br_2$ requires C, 32·1; H, 2·4; Br, 47·6%).

Similar esters were obtained when chloral was allowed to interact with 2 : 4-dibromophenylhydrazine, 2-chloro-4-bromophenylhydrazine, and 4-chloro-2-bromophenylhydrazine in presence of alcohols and were all found to be identical with the corresponding esters prepared from glyoxylic acid.

Ethyl glyoxylate 2 : 4-*dibromophenylhydrazone* crystallises in slender, pale yellow, flattened prisms, m. p. 119° (Found: Br, 45·6. $C_{10}H_{10}O_2N_2Br_2$ requires Br, 45·7%), n-*propyl glyoxylate* 2 : 4-*dibromophenylhydrazone* in short, pale yellow, flattened prisms, m. p. 75° (Found: Br, 44·0. $C_{11}H_{12}O_2N_2Br_2$ requires Br, 43·9%), and *ethyl glyoxylate* 2-*chloro*-4-*bromophenylhydrazone* (Found: Cl, 11·6; Br, 26·3. $C_{10}H_{10}O_2N_2ClBr$ requires Cl, 11·6; Br, 26·2%) and *ethyl glyoxylate* 4-*chloro*-2-*bromophenylhydrazone* in slender, pale yellow prisms, m. p. 120° and 115°, respectively.

Glyoxylic Acid 2 : 4-*Dichlorophenylhydrazone.*—Glyoxylic acid (made by the electrolytic reduction of oxalic acid) and 2 : 4-dichlorophenylhydrazine hydrochloride reacted at once in aqueous solution at 60° and the *hydrazone* separated as a yellow solid. It is sparingly soluble in water, very easily soluble in alcohol, and crystallises from hot aqueous alcohol in pale yellow needles, decomp. about 150° (Found: Cl, 30·3. $C_8H_6O_2N_2Cl_2$ requires Cl, 30·4%).

The 2 : 4-*dibromophenylhydrazone* of glyoxylic acid resembles the dichloro-hydrazone very closely. It crystallises in pale yellow needles, decomp. about 150° (Found: Br, 49·5. $C_8H_6O_2N_2Br_2$ requires Br, 49·7%).

Action of 2 : 4-*Dichlorophenylhydrazine Hydrochloride on Bromal dissolved in Ethyl Alcohol.*—A mixture of 11 g. of 2 : 4-dichlorophenylhydrazine hydrochloride, 14 g. of bromal, and 100 c.c. of ethyl alcohol was boiled under reflux for an hour, hydrogen bromide being liberated in quantity and ethyl bromide (recognisable by its odour) formed. The bright yellow liquid obtained, on cooling, deposited ethyl glyoxylate 2 : 4-dichlorophenylhydrazone, m. p. 121·5°, identical in every respect with that prepared both from chloral and from glyoxylic acid.

Methyl glyoxylate 2 : 4-dibromophenylhydrazone, m. p. 136°, was similarly obtained when 2 : 4-dibromophenylhydrazine hydrochloride was heated with bromal dissolved in methyl alcohol.

Action of 2 : 4-*Dichlorophenylhydrazine Hydrochloride on Chloral Hydrate dissolved in Acetic Acid or Water.*—To a solution of 16·5 g. (1 mol.) of chloral hydrate in 100 c.c. of acetic acid, 21·5 g. (1 mol.)

of 2 : 4-dichlorophenylhydrazine hydrochloride and 33 g. of anhydrous sodium acetate (4 mols.) were added. The liquid became pale yellow, but little apparent change occurred until the temperature was raised to about 60°; obvious action then took place and the liquid became bright red. It was heated on a water-bath for ½ hour to complete the reaction and poured into water; *αα-dichloro-β-2 : 4-dichlorobenzeneazoethylene* (IV) then separated as a scarlet-red solid.

If aqueous solutions of equivalent quantities of chloral hydrate and 2 : 4-dichlorophenylhydrazine hydrochloride are mixed and slowly heated, the same compound separates at about 80° as a crimson, viscid liquid which solidifies on cooling and from which the supernatant liquid, now strongly acid from the hydrogen chloride set free in the reaction, can be decanted.

The red solid is readily soluble in boiling chloroform, acetic acid, and alcohol, and separates from warm alcohol in slender, flattened, golden-red prisms, m. p. 84·5° (Found : C, 35·6; H, 1·6; N, 10·2; Cl, 52·5; *M*, cryoscopic in benzene, 262. $C_8H_4N_2Cl_4$ requires C, 35·6; H, 1·5; N, 10·4; Cl, 52·6%; *M*, 270). It does not react with acetic anhydride. When it was boiled with ethyl alcohol for 8 hours, a deep orange-coloured liquid was obtained from which, on cooling, ethyl glyoxylate 2 : 4-dichlorophenylhydrazone separated.

Action of Bromine upon αα-Dichloro-β-2 : 4-dichlorobenzeneazoethylene.—To a solution of 5 g. (1 mol.) of αα-dichloro-β-2 : 4-dichlorobenzeneazoethylene in 20 c.c. of warm acetic acid, 3·5 g. (1 mol.) of bromine in 5 c.c. of acetic acid were added. The bromine slowly disappeared and the solution became paler in colour. The solution was then poured into water; *αα-dichloro-β-bromo-β-2 : 4-dichlorobenzeneazoethylene* (V) separated as a brownish-red solid. It is easily soluble in warm acetic acid or alcohol and separates in small, red needles, m. p. 90° (Found : Cl, 40·5; Br, 22·7. $C_8H_3N_2Cl_4Br$ requires Cl, 40·7; Br, 22·9%).

αα-Dichloro-β-2 : 4-dibromobenzeneazoethylene crystallises in slender, orange-red, flattened prisms, m. p. 96·5° (Found : Cl, 19·9; Br, 44·9. $C_8H_4N_2Cl_2Br_2$ requires Cl, 19·8; Br, 44·6%), *αα-dichloro-β-2-chloro-4-bromobenzeneazoethylene* in small, slender, orange-red prisms, m. p. 84° (Found : Cl, 33·6; Br, 25·3. $C_8H_4N_2Cl_3Br$ requires Cl, 33·8; Br, 25·4%), and *αα-dichloro-β-4-chloro-2-bromobenzeneazoethylene* in slender, orange-red prisms, m. p. 81°.

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CCCLXXXII.—*The Halogenation of* p-*Hydroxydiphenylamine. Part II.*

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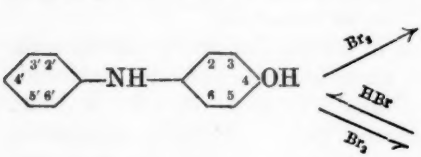
The main reaction between bromine or chlorine and *p*-hydroxydiphenylamine and its derivatives (Smith and Orton, J., 1908, **93**, 314) may follow one of two paths, leading either to a halogen-substituted *p*-hydroxydiphenylamine (A) or to a quinoneanil (benzoquinonephenylimine) (B). More drastic treatment leads to a disruption of the molecule.



$C_{12}H_{10}NOBr + HBr$ (A)

$C_6H_5{\cdot}N{:}C_6H_4{:}O + 2HBr$ (B)

The bromination of *p*-hydroxydiphenylamine, which is very rapid (*loc. cit.*), indicates that the imino-group is much more powerful as a directing group than the hydroxyl, the 2 : 2′ : 4′-trisubstituted compound being the first isolable product. The influence of the imino-group is then diminished and bromine enters successively into positions 5 and 3, and, finally, positions 6 and 6′ simultaneously. It is now found that, when the hydroxyl group is previously esterified by means of benzoyl chloride or *p*-toluenesulphonyl chloride, the 4′-bromo-, 2 : 2′ : 4′-tribromo-, and, finally, 2 : 6 : 2′ : 4′ : 6′-pentabromo-compounds are successively obtained.

In acetic acid, the first main action of bromine on 2 : 6 : 2′ : 4′ : 6′-pentabromohydroxydiphenylamine is oxidation to the quinoneanil. The reaction is reversible and, provided the hydrogen bromide formed is not removed, an equilibrium is reached. The small amount of the hydroxy-compound present undergoes slow nuclear substitution (irreversible), displacing the equilibrium, and in time the whole is converted into the 2 : 3 : 5 : 6 : 2′ : 4′ : 6′-heptabromohydroxy-derivative, the original violet colour of the solution fading as the quinoneanil is reduced by the hydrogen bromide and brominated. If the hydrogen bromide be removed by the addition of sodium acetate, reduction and bromination are prevented.

Chlorine has a disruptive action on *p*-hydroxydiphenylamine; the benzoate or *p*-toluenesulphonate, however, may be chlorinated by the chloroamine method (Orton and King, J., 1911, **99**, 1185; Orton and Bradfield, this vol., p. 986), the reaction following a similar

course to that of bromination of the esters, yielding finally the 2 : 6 : 2′ : 4′ : 6′-pentachloro-compound. The rate of further substitution in 2 : 6 : 2′ : 4′ : 6′-pentachloro-*p*-hydroxydiphenylamine, obtained from the ester, has now become so diminished that when it is treated with chlorine, oxidation to the quinoneanil initially predominates. This is succeeded, however, by reduction and substitution as in the further bromination of pentabromohydroxydiphenylamine, yielding the 2 : 3 : 6 : 2′ : 4′ : 6′-hexachloro- and 2 : 3 : 5 : 6 : 2′ : 4′ : 6′-heptachloro-derivatives.

The action of hydrochloric acid on an acetic acid solution of the pentachloroquinoneanil obtained by oxidation of pentachlorohydroxydiphenylamine with chromic anhydride or mercuric oxide yields the same hexa- and hepta-chloro-compounds. This fact is entirely in harmony with the view of the course of the reaction of *p*-hydroxydiphenylamine derivatives with halogens which has been put forward above; in so far as it relates to the production of halogenated derivatives from the quinoneanil, it closely resembles the scheme first advanced by Wichelhaus (*Ber.*, 1879, **12**, 1500) to explain the action of hydrochloric acid on quinone.

Several mixed chlorobromo-*p*-hydroxydiphenylamine derivatives have been prepared.

Amongst the properties of the halogen derivatives of *p*-hydroxydiphenylamine, certain anomalies appear for which at present no explanation can be offered. These are :

(1) The majority of the compounds are, as would be expected, soluble in aqueous alkali; but the following are not, although they are soluble in alcoholic potash : 2 : 2′ : 4′-trichloro-5 : 6′-dibromo-, 2 : 5 : 2′ : 4′-tetrabromo-, 2 : 2′ : 4′-trichloro-3 : 5 : 6 : 6′-tetrabromo-, 2 : 3 : 5 : 2′ : 4′-pentabromo-, 2 : 3 : 5 : 2′ : 4′ : 6′-hexabromo-, 2 : 3 : 5 : 2′ : 4′ : 6′-hexachloro- and heptabromo-*p*-hydroxydiphenylamine.

Further, these same compounds have resisted all attempts at sulphonylation with *p*-toluenesulphonyl chloride, not only by the Schotten–Baumann procedure, but in pyridine or quinoline, in which they are soluble, indicating that the phenomenon, although concomitant, is not attributable simply to insolubility.

(2) Although 2 : 5 : 2′ : 4′-tetrabromo- and 2 : 3 : 5 : 2′ : 4′-pentabromo-*p*-hydroxydiphenylamine react with bromine, the benzoyloxy-derivatives prepared from them react very slowly or not at all under the conditions usually successful, in spite of the fact that positions ortho to the imino-group remain vacant, *i.e.*, esterification not only retards substitution in the ortho-position to the hydroxyl group, but greatly diminishes the reactivity of the molecule as a whole, even transmitting the effect through nitrogen to an attached

benzene ring. It is hoped to study this observation, which appears to be unique, in greater detail.

EXPERIMENTAL.

In the preparation of *p*-hydroxydiphenylamine by Calm's method (*Ber.*, 1883, **16**, 2786; 1884, **17**, 2431) the yield is much improved by the employment of crude aniline, and both yield and purity are enhanced if pure aniline to which a drop of sulphuric acid has been added is used. The product, after distillation in superheated steam and then under 12 mm. pressure, melts at 73°.

The p-*toluenesulphonyl* derivative, prepared from *p*-toluenesulphonyl chloride (210 g.), *p*-hydroxydiphenylamine (185 g.), benzene (900 c.c.), and aqueous sodium hydroxide, crystallises from alcohol in thin plates, m. p. 126·5°, soluble in benzene and chloroform, less soluble in alcohol, petroleum, and acetic acid (Found: S, 9·5. $C_{19}H_{17}O_3NS$ requires S, 9·5%).

The acetic acid used as a medium for halogenation was purified by Orton and Bradfield's method (this vol., p. 983).

Chloro-compounds.

The following chloro-4-acyloxydiphenylamines were prepared by chlorination by the chloroamine (*N* : 2 : 4-trichloroacetanilide or dichloramine T) method and were usually precipitated on addition of water. They were hydrolysed by boiling alcoholic potassium hydroxide, and the hydroxy-compounds precipitated by addition of water to the acidified solutions. The anils were prepared by oxidising the corresponding chlorohydroxydiphenylamines in boiling benzene with yellow mercuric oxide or in boiling acetic acid with chromic acid; they were usually isolated by evaporation of the solvent and addition of petroleum in the former method and by addition of water in the latter. Fission of the anils was effected in acetic acid by addition of sulphuric acid; on dilution with water and basification, the expected chloroaniline was obtained in every case.

4′-*Chloro*-4-*benzoyloxydiphenylamine* is prepared from *p*-benzoyloxydiphenylamine; the reaction, initiated by the addition of one drop of hydrochloric acid, is completed in 15 minutes. The product (yield, 30%) crystallises from petroleum or 98% acetic acid in silvery plates, m. p. 148·5°. The presence of isomerides is indicated (Found: Cl, 10·6. $C_{19}H_{14}O_2NCl$ requires Cl, 11·0%).

4′-*Chloro*-4-*hydroxydiphenylamine* forms pale green leaflets (yield, 72%), m. p. 91° (Found: Cl, 15·9. $C_{12}H_{10}ONCl$ requires Cl, 16·2%). The p-*toluenesulphonate* has m. p. 93—94° (Found: Cl, 9·3. $C_{19}H_{16}O_3NClS$ requires Cl, 9·5%).

4′-*Chlorobenzoquinoneanil* crystallises in dark red, massive prisms,

m. p. 83·5°, insoluble in water, sparingly soluble in alcohol, hot or cold, and in cold petroleum and acetic acid, readily soluble in chloroform and benzene (Found: Cl, 16·0. $C_{12}H_8ONCl$ requires Cl, 16·3%).

2 : 2′ : 4′-*Trichloro*-4-*benzoyloxy*- and -4-p-*toluenesulphonyloxy*-*diphenylamines* are prepared at 50—55° from the 4-acyloxy-compounds or their monochloro-derivatives and separate on cooling. The *benzoyloxy*-compound has m. p. 114° (Found: Cl, 27·3. $C_{19}H_{12}O_2NCl_3$ requires Cl, 27·1%); the *toluenesulphonyloxy*-compound crystallises from hot benzene–petroleum or from acetic acid in prisms, m. p. 130·5° (Found: Cl, 24·3. $C_{19}H_{14}O_3NCl_3S$ requires Cl, 24·1%).

2 : 2′ : 4′-*Trichloro*-4-*hydroxydiphenylamine*, crystallised from glacial acetic acid and then from petroleum, forms prisms, never quite colourless, m. p. 128° (Found: Cl, 36·7. $C_{12}H_8ONCl_3$ requires Cl, 36·9%).

2 : 2′ : 4′-*Trichlorobenzoquinoneanil* separates from petroleum (b. p. 40—60°), containing a very little benzene, in long, bronzy needles, m. p. 72·5°. It is readily soluble in all organic solvents except light petroleum (Found: Cl, 37·1. $C_{12}H_6ONCl_3$ requires Cl, 37·2%).

2 : 6 : 2′ : 4′-*Tetrachloro*-4-p-*toluenesulphonyloxydiphenylamine* is obtained from the trichlorotoluenesulphonyloxydiphenylamine at 45—50°, and is separated from the other isomerides produced only by a tedious series of fractional precipitations from chloroform and light petroleum. It is much more soluble in common solvents than the tri- and penta-chloro-derivatives, and crystallises from acetic acid, chloroform, and petroleum (b. p. 110°) in prisms, m. p. 126° (Found: Cl, 30·1. $C_{19}H_{13}O_3NCl_4S$ requires Cl, 29·8%).

The *tetrachlorohydroxy*-compound solidifies with difficulty, but after being thoroughly washed and dried it may be obtained crystalline by the addition of petroleum, b. p. 40—60°, to a solution in petroleum, b. p. 110°; it then melts at 113° (Found: Cl, 44·3. $C_{12}H_7ONCl_4$ requires Cl, 44·0%). The *tetrachlorobenzoyloxy*-compound is obtained by benzoylating the tetrachlorohydroxy-compound in pyridine; after crystallisation from petroleum (b. p. 60—85°) it melts at 114·5° (Found: Cl, 33·1. $C_{19}H_{11}O_2NCl_4$ requires Cl, 33·3%).

2 : 6 : 2′ : 4′-*Tetrachlorobenzoquinoneanil* separates from ethyl acetate in violet crystals, m. p. 143° (Found: Cl, 44·5. $C_{12}H_5ONCl_4$ requires Cl, 44·2%).

2 : 6 : 2′ : 4′ : 6′-*Pentachloro*-4-*benzoyloxydiphenylamine* is prepared from the mono- or trichloro-derivative; after crystallisation from alcohol (yield, 62%) it melts at 133—134° (Found: Cl, 38·0. $C_{19}H_{10}O_2NCl_5$ requires Cl, 38·4%). The *toluenesulphonyloxy*-compound is prepared from the trichlorosulphonyloxy-compound

at 55°; on cooling, it separates in quantitative yield, in prisms, m. p. 156·5°, unaltered by crystallisation from acetic acid. It is also obtained by passing chlorine into a hot acetic acid solution of 4-*p*-toluenesulphonyloxydiphenylamine in presence of anhydrous sodium acetate. It is soluble in chloroform, but sparingly soluble in other solvents (Found: Cl, 34·7. $C_{19}H_{12}O_3NCl_5S$ requires Cl, 34·7%). The *pentachlorohydroxy*-compound crystallises from petroleum in clear brown prisms, m. p. 156° (Found: Cl, 49·2. $C_{12}H_6ONCl_5$ requires Cl, 49·6%). The *monoacetyl* derivative, obtained by treating the hydroxy-compound in acetic acid with acetic anhydride in the presence of sodium acetate, has m. p. 126°. It is insoluble in alkali, very soluble in benzene, petroleum, and chloroform, and sparingly soluble in acetic acid (Found: Cl, 44·0. $C_{14}H_8O_2NCl_5$ requires Cl, 44·4%).

2 : 6 : 2′ : 4′ : 6′-*Pentachlorobenzoquinoneanil* (prepared by the chromic acid method) forms fine, bronzy-red needles with a metallic lustre, m. p. 163° (Found: Cl, 49·5. $C_{12}H_4ONCl_5$ requires Cl, 49·9%).

All attempts to chlorinate further *p*-benzoyloxy- and 4-*p*-toluenesulphonyloxy-diphenylamine have been unsuccessful, as is to be expected.

2 : 3 : 6 : 2′ : 4′ : 6′-*Hexachloro*-4-*hydroxydiphenylamine* is prepared from pentachlorohydroxydiphenylamine and forms hemispherical nodules, m. p. 114° (Found: Cl, 53·6. $C_{12}H_5ONCl_6$ requires Cl, 54·3%). Benzoylation in pyridine gives the *benzoyloxy*-derivative, which, crystallised from alcohol and then from petroleum, forms small clusters of hard, glistening, brown prisms, m. p. 125° (Found: Cl, 42·5. $C_{19}H_9O_2NCl_6$ requires Cl, 42·9%). The *toluenesulphonyloxy*-derivative crystallises from glacial acetic acid in white prisms, m. p. 141° (Found: Cl, 39·0. $C_{19}H_{11}O_3NCl_6S$ requires Cl, 39·0%).

2 : 3 : 6 : 2′ : 4′ : 6′-*Hexachlorobenzoquinoneanil* * is obtained by the

* The synthesis of this compound establishes the hitherto uncertain constitution of the isomeride yielding the same fission products which was obtained by Orton and Smith (J., 1905, **87**, 389) as a product of the transformation of *s*-trichlorophenylnitroamine, as the 2 : 3 : 5 : 2′ : 4′ : 6′-compound. Similarly, the preparation of 2 : 6 : 2′ : 4′ : 6′-pentabromobenzoquinoneanil (p. 2861) establishes the constitution of the isomeride produced by transformation of *s*-tribromophenylnitroamine (Orton and Smith, J., 1907, **91**, 146) as the 3 : 5 : 2′ : 4′ : 6′-pentabromo-compound. It is regretted that, owing to a clerical error, the melting points of the penta- and hexa-bromobenzoquinoneanils given in that paper have become interchanged. Further examination has shown that the hexabromoquinoneanil then obtained was not completely pure. The following corrected melting points are given to avoid ambiguity:

3 : 5 : 2′ : 4′ : 6′-Pentabromo-4-hydroxydiphenylamine, m. p. 157°.

3 : 5 : 2′ : 4′ : 6′-Pentabromobenzoquinoneanil, m. p. 150·5°.

2 : 3 : 5 : 2′ : 4′ : 6′-Hexabromo-4-hydroxydiphenylamine, m. p. 216°.

2 : 3 : 5 : 2′ : 4′ : 6′-Hexabromobenzoquinoneanil, m. p. 171°.

chromic acid method as a black, crystalline solid, m. p. 114° after recrystallisation from alcohol. It dissolves in ordinary solvents, except alcohol, to give violet solutions (Found: Cl, 54·2. $C_{12}H_3ONCl_6$ requires Cl, 54·65%). On treatment of the red-brown solution in sulphuric acid (1 in 100) with water, the colour changes to light yellow and a mixture of yellow plates and red needles separates. The mixture is collected and digested with a little cold alcohol; the yellow trichlorobenzoquinone remaining undissolved melts, after crystallisation from hot alcohol, at 162—163°. Careful dilution of the alcoholic extract gave *s*-trichloroaniline, m. p. 77·5° (acetyl derivative, m. p. 204°).

Heptachloro-4-hydroxydiphenylamine.—The pentachlorohydroxydiphenylamine (5 g.; 1 mol.) in 15 c.c. of acetic acid is treated with a solution of *N*-chloroacetamide (1·35 g.; 1 mol.) in 5 c.c. of the same solvent, together with two drops of 20% hydrochloric acid, the mixture becoming at once deep violet. After 1 hour, a like amount of chloroamine is added. No chlorine remains after 18 hours. The solution is decolorised by heating with zinc dust and the boiling suspension is filtered at once. White needles (55%) separate on cooling, m. p. 158—159°, unchanged on recrystallisation from petroleum or slightly diluted acetic acid (Found: Cl, 58·05. $C_{12}H_4ONCl_7$ requires Cl, 58·3%).

The *benzoyloxy*-derivative crystallises from glacial acetic acid in massive, white plates, m. p. 164° (Found: Cl, 46·5. $C_{19}H_8O_2NCl_7$ requires Cl, 46·8%). The sulphonylation of the heptachlorohydroxy-derivative is characterised by its slowness, due no doubt to the presence of two ortho-substituents. After 45 minutes' shaking, a violet solid has separated; after being washed with water and with benzene, it crystallises from glacial acetic acid in white needles, m. p. 141·5° (Found: Cl, 42·4. $C_{19}H_{10}O_3NCl_7S$ requires Cl, 42·8%).

Heptachlorobenzoquinoneanil separates from alcohol in small, black crystals, m. p. 114°. Its solutions are violet. Fission by dilute sulphuric acid (1 in 50) and addition of water gives successively tetrachlorobenzoquinone (which sublimes in pale yellow, iridescent plates, not molten at 260°) and *s*-trichloroaniline, m. p. 77·5°.

Action of Hydrochloric Acid on 2 : 6 : 2′ : 4′ : 6′-Pentachlorobenzoquinoneanil.—Concentrated hydrochloric acid (2 c.c.) was added to the quinoneanil (1·5 g.) in glacial acetic acid (100 c.c.). After 18 hours, the bluish-green solution was treated with zinc dust to remove the excess of hydrochloric acid, filtered, and diluted with 300—400 c.c. of water. Hexachlorohydroxydiphenylamine separated as white, crystalline crusts, m. p. 114° after recrystallisation. The action of hydrochloric acid on 2 : 3 : 6 : 2′ : 4′ : 6′-hexachlorobenzo-

quinoneanil in a similar manner yielded heptachlorohydroxydiphenylamine.

Bromo-compounds.

4′-Bromo-4-benzoyloxydiphenylamine. — *p*-Benzoyloxydiphenylamine (5 g.; 1 mol.) and anhydrous sodium acetate (2 mols.), dissolved in 250 c.c. of acetic acid, were treated with a solution of bromine (0·865 c.c.; 1 mol.) in 125 c.c. of acetic acid. After ½ hour, dilution to 75% caused slow separation of white, fibrous needles, which, after crystallisation from alcohol or benzene–ligroin, melted at 150·5°: yield, 33% (Found: Br, 21·2. $C_{19}H_{14}O_2NBr$ requires Br, 21·7%).

By hydrolysis of the above, the *hydroxy*-compound was obtained as thin laminæ, m. p. 108°, in 75% yield (Found: Br, 29·7. $C_{12}H_{10}ONBr$ requires Br, 30·3%).

4′-Bromobenzoquinoneanil was obtained by oxidation of the hydroxy-compound with excess of yellow mercuric oxide. The solution was evaporated to a small volume and the quinoneanil then separated in scarlet crystals, m. p. 100—104°. The melting point of this substance, which appears to be dimorphic, is not sharp and depends on the nature and temperature of the solvent (Found: Br, 29·8. $C_{12}H_8ONBr$ requires Br, 30·5%). Fission gave *p*-bromoaniline, but no trace of *p*-benzoquinone was found.

2 : 2′ : 4′-Tribromo-4-p-toluenesulphonyloxydiphenylamine was prepared, by the method described above, from 4-*p*-toluenesulphonyloxydiphenylamine at 50°, and crystallised from benzene–petroleum, acetone, or glacial acetic acid (Found: Br, 41·7; S, 5·6. $C_{19}H_{14}O_3NBr_3S$ requires Br, 41·7; S, 5·5%). The tribromo-4-benzoyloxy-compound obtained by Smith and Orton (*loc. cit.*) is produced in better yield by the Schotten–Baumann method or by bromination of *p*-benzoyloxydiphenylamine. Both esters are sparingly soluble in common organic media, and give on hydrolysis the tribromohydroxydiphenylamine described by Smith and Orton (*loc. cit.*), this synthesis providing the further evidence required to establish it as *2 : 2′ : 4′-tribromo-4-hydroxydiphenylamine.*

The low solubility of tribromoacyloxydiphenylamines necessitated the following procedure: Finely powdered tribromo-4-*p*-toluenesulphonyloxydiphenylamine was exposed to the vapour of bromine in the presence of anhydrous sodium phosphate or sodium borate, and after 20 hours the absorbed bromine was removed by evacuation. Extraction with boiling benzene gave a quantitative yield of white, prismatic crystals of the sparingly soluble *2 : 6 : 2′ : 4′ : 6′-pentabromo-4-p-toluenesulphonyloxydiphenylamine*, m. p. 210° (Found: Br, 54·1. $C_{19}H_{12}O_3NBr_5S$ requires Br, 54·5%).

The *hydroxy*-compound (yield, 60%) crystallised from ligroin containing 5% of benzene, or from 75% alcohol, in massive, brown prisms, m. p. 206—207° (Found : Br, 68·5. $C_{12}H_6ONBr_5$ requires Br, 69·0%). The *benzoyloxy*-derivative, prepared by benzoylation in pyridine, separated after 24 hours and was precipitated from benzene solution by light petroleum in white needles, m. p. 141—142° (Found : Br, 58·6. $C_{19}H_{10}O_2NBr_5$ requires Br, 58·5%).

2 : 6 : 2′ : 4′ : 6′-*Pentabromobenzoquinoneanil*, prepared by the chromic acid method, has m. p. 184—185° (Found : Br, 68·7. $C_{12}H_4ONBr_5$ requires Br, 69·2%). Fission gave *s*-tribromoaniline and 2 : 6-dibromobenzoquinone.

Pentabromo-4-hydroxydiphenylamine with bromine in acetic acid solution in the absence of an absorbent for hydrogen bromide, yielded heptabromohydroxydiphenylamine (Smith and Orton, *loc. cit.*), but in the presence of sodium acetate oxidation to the violet quinoneanil occurred. An attempt to sulphonylate the heptabromohydroxy-compound by the Schotten–Baumann method gave a *substance*, m. p. 188°, soluble in 5% alcoholic potash, which was neither the initial material nor the desired sulphonyloxy-compound (Found : Br, 70·4%).

All attempts to sulphonylate 2 : 5 : 2′ : 4′-tetrabromo- and 2 : 3 : 5 : 2′ : 4′-pentabromo-4-hydroxydiphenylamine (Smith and Orton, *loc. cit.*) by the Schotten–Baumann procedure and the various modifications of Einhorn's method (compare Fischer and Pfaehler, *Ber.*, 1920, **53**, 1642; Ohle, *Ber.*, 1924, **57**, 409; Ohle and Dickhäuser, *Ber.*, 1925, **58**, 2593) failed.

In general, the sulphonyloxy-compounds are brominated more smoothly than the benzoyloxy-compounds, but the failure to sulphonylate the two hydroxy-compounds above led us to investigate the effect of bromine on the corresponding benzoyloxydiphenylamines. Although two positions ortho to the powerfully directing imino-group are present in 2 : 5 : 2′ : 4′-tetrabromo-4-benzoyloxydiphenylamine, this substance brominates too slowly to permit isolation of higher derivatives. Prolonged refluxing with bromine in carbon tetrachloride solution is followed by recovery of initial material. More drastic conditions such as the gaseous bromine–sodium phosphate method, or in chloroform in the presence of ferric chloride, lead to complete disruption of the molecule. Somewhat similar results followed from the work on 2 : 3 : 5 : 2′ : 4′-pentabromo-4-benzoyloxydiphenylamine, but gaseous bromine converted it into a viscous, dark liquid from which a small amount of heptabromobenzoyloxydiphenylamine was isolated.

Chlorobromo-compounds.

6 : 6′-*Dichloro*-2 : 2′ : 4′-*tribromo*-4-p-*toluenesulphonyloxy-* and -4-*benzoyloxy-diphenylamines.*—Because of low solubility, the tribromo-4-acyloxydiphenylamines were chlorinated in suspension in acetic acid solutions of dichloramine T (100% excess); after 18 hours, 2 equivalents of chlorine had disappeared, a quantitative yield of pentahalogenated derivative having separated.

The *sulphonyloxy*-compound melted, after crystallisation from petroleum, at 185° (Found: * Hals., 131·2; AgCl, 111·6. $C_{19}H_{12}O_3NCl_2Br_3S$ requires Hals., 131·9; AgCl, 111·3). The *benzoyloxy*-compound, after crystallisation from acetic acid, melted at 153° (Found: Hals., 140·9; AgCl, 119. $C_{19}H_{10}O_2NCl_2Br_3$ requires Hals., 143; AgCl, 120·6). Both esters are very sparingly soluble in all solvents. Hydrolysis of these gave the *hydroxy*-compound in small, brown prisms which, after twice crystallising from petroleum, melted at 166° (Found: Hals., 171·6; AgCl, 145·1. $C_{12}H_6ONCl_2Br_3$ requires Hals., 173·1; AgCl, 146·1).

6 : 6′-*Dichloro*-2 : 2′ : 4′-*tribromobenzoquinoneanil*, obtained by the chromic acid method, crystallised from acetic acid in deep purple, irregular prisms, m. p. 150° (Found: Hals., 173·1; AgCl, 147·8. $C_{12}H_4ONCl_2Br_3$ requires Hals., 174·0; AgCl, 146·6). By careful dilution of its solution in concentrated sulphuric acid, 2-chloro-4 : 6-dibromoaniline was obtained.

2 : 2′ : 4′-*Trichloro*-6 : 6′-*dibromo*-4-p-*toluenesulphonyloxydiphenylamine.*—Trichlorosulphonyloxydiphenylamine was brominated by the bromine vapour–sodium borate (phosphate) method. After crystallisation from benzene, chloroform, or petroleum, the product melted at 174°. Yield, quantitative (Found: Hals., 133·5; AgCl, 120·1. $C_{19}H_{12}O_3NCl_3Br_2S$ requires Hals., 134·3; AgCl, 119·5). The *benzoyloxy*-compound, prepared similarly, formed a sticky magma, which was suspended in acetic acid and freed from bromine by passage of sulphur dioxide. On warming, the material dissolved, and then separated in colourless prisms, m. p. 134° (Found: Hals., 149·6; AgCl, 133·8. $C_{19}H_{10}ONCl_3Br_2$ requires Hals., 146·5; AgCl, 130·8). The *hydroxy*-compound, after repeated crystallisation from 75% acetic acid, formed irregular prisms, m. p. 180°, readily soluble in all other organic solvents (Found: Hals., 176·5; AgCl, 157·8. $C_{12}H_6ONCl_3Br_2$ requires Hals., 180·5; AgCl, 160·9).

* For the Carius estimation of some of the substances here described, prolonged heating at 300° was required. In such cases, Robertson's method (J., 1915, **107**, 902) frequently proved of service. For the analysis of the chlorobromo-compounds, the mixture of silver halides (the weight of which, obtained from 100 parts of the substance, is denoted by "Hals.") obtained was usually converted into silver chloride by warming in a current of chlorine.

By the chromic acid method 2 : 2′ : 4′-*trichloro*-6 : 6′-*dibromobenzoquinoneanil* was obtained in massive, black prisms, m. p. 170° after crystallisation from chloroform (Found : Hals., 181·8; AgCl, 162·5. $C_{12}H_4ONCl_3Br_2$ requires Hals., 181·4; AgCl, 161·6). The fission of this quinoneanil requires care : a solution of 0·25 g. in 25 c.c. of concentrated sulphuric acid was slowly diluted with water to 20%. A small quantity of solid (unexamined) separated, and ether extraction then removed 2 : 4-dichloro-6-bromoaniline, m. p. 78° (acetyl derivative, m. p. 217°). Chattaway and Orton (J., 1901, 79, 816) give m. p. 83° and 218°, respectively.

2 : 2′ : 4′-*Trichloro*-5-*bromo*-4-*hydroxydiphenylamine*.—Trichlorohydroxydiphenylamine in acetic acid solution containing sodium acetate was oxidised by bromine, giving quinhydrone-like complexes, but their formation was avoided when 1·85 c.c. of bromine in 25 c.c. of chloroform were added to 10 g. of the amine in 100 c.c. of boiling chloroform during 1 hour; evolution of hydrogen bromide ceased after 2·5 hours. The solution, concentrated to 25—30 c.c., deposited matted needles which, after crystallisation from petroleum, melted at 127—128° (yield, 5·9 g.); a further 2 g. were recovered from the mother-liquor (combined yields, 60%). The compound is easily soluble in aqueous caustic soda (Found : Hals., 165·0; AgCl, 152·8. $C_{12}H_7ONCl_3Br$ requires Hals., 167·4; AgCl, 155·3). The *benzoyloxy*-compound separated from pyridine; m. p. 186° (Found : Hals., 129·4; AgCl, 120·0. $C_{19}H_{11}O_2NCl_3Br$ requires Hals., 131·2; AgCl, 121·7).

When the above hydroxy-compound was sulphonylated in the usual way, and the reaction product kept for 2 hours in a freezing-mixture, a red, crystalline solid separated. Following washing with water and with light petroleum, crystallisation from slightly diluted acetic acid gave colourless prisms of 2 : 2′ : 4′-*trichloro*-5-*bromo*-4-*sulphonyloxydiphenylamine*, m. p. 114° (Found : Hals., 117·9; AgCl, 109·5. $C_{19}H_{13}O_3NCl_3BrS$ requires Hals., 119·0; AgCl, 110·1).

2 : 2′ : 4′-*Trichloro*-5-*bromobenzoquinoneanil* (mercuric oxide method) crystallised from benzene or petroleum, or a mixture of the two, in hemispherical nodules of red, spear-shaped needles, m. p. 115°. Fission by solution in 45 volumes of concentrated sulphuric acid and slow dilution to 25% strength, followed by steam distillation, gave a yellow quinone, m. p. 172°, reduction of which by sulphur dioxide in aqueous-alcoholic solution gave a colourless quinol, m. p. 169° (2-chloro-5-bromobenzoquinone and 2-chloro-5-bromoquinol both melt at 172°). Neutralisation of the acid liquor, followed by distillation in steam, gave 2 : 4-dichloroaniline, m. p. 61° (acetyl derivative, m. p. 145°).

2 : 2′ : 4′-*Trichloro*-5 : 6′-*dibromo*-4-*hydroxydiphenylamine*, prepared

by refluxing trichlorobromohydroxydiphenylamine (10 g.) and bromine (1 mol.) in 80 c.c. of chloroform for 90 minutes, separated, on cooling, in white needles, m. p. 189° after two crystallisations from chloroform (Found: Hals., 176·9; AgCl, 160·5. $C_{12}H_6ONCl_3Br_2$ requires Hals., 180·5; AgCl, 160·9). Fractions obtained from the chloroform mother-liquor appeared to contain isomerides. Attempts to sulphonylate and benzoylate this substance failed.

2 : 2′ : 4′-*Trichloro*-5 : 6′-*dibromobenzoquinoneanil* (chromic acid method) formed small, vermilion, scintillating needles, m. p. 133° (Found: Hals., 177·7; AgCl, 159·1. $C_{12}H_4ONCl_3Br_2$ requires Hals., 181·4; AgCl, 161·4). Fission gave golden-yellow plates, m. p. 165° (2-chloro-5-bromobenzoquinone melts at 172°), and on dilution to 20% strength 2 : 4-dichloro-6-bromoaniline was precipitated.

2 : 2′ : 4′-*Trichloro*-3 : 5 : 6 : 6′-*tetrabromo*-4-*hydroxydiphenylamine*.—To a solution of 4 g. of trichlorohydroxydiphenylamine in 40 c.c. of chloroform boiling under reflux, 2·8 c.c. (4 mols.) of bromine in the same solvent were slowly added; hydrogen bromide was at first rapidly evolved. The mixture was then transferred to a silica flask, with excess of bromine, and exposed to sunlight for 3½ days, the solid that had separated after 12 hours being redissolved by gentle warming. The large, thin laminæ (3·9 g.) which separated were broken up, and freed from bromine and chloroform over charcoal and potash in a vacuum; m. p. 160°. Evaporation of the mother-liquor yielded a further 3·5 g. (combined yield, 89%) (Found: Hals., 194·5; AgCl, 165·1. $C_{12}H_4ONCl_3Br_4$ requires Hals., 195·7; AgCl, 166·2). The *benzoyloxy*-compound crystallised from chloroform–acetic acid in small, elongated prisms, m. p. 163° (Found: Hals., 169·8. $C_{19}H_8O_2NCl_3Br_4$ requires Hals., 169·7). Attempts to sulphonylate the hydroxy-compound failed.

2 : 2′ : 4′-*Trichloro*-3 : 5 : 6 : 6′-*tetrabromobenzoquinoneanil* (chromic acid method) crystallised from acetic acid in slender, indigo needles, m. p. 136°. Fission and dilution gave a very sparingly soluble substance, m. p. 294°, and 2 : 4-dichloro-6-bromoaniline. The literature notes the insolubility of chlorotribromoquinone and records two values for its m. p., *viz.*, 292° and 303°.

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CCCLXXXIII.—*Substitution Products of 4-Hydroxybenzophenone and of its Methyl Ether.*

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THE orientation of substituents in the benzophenone series has been investigated in but few cases, *e.g.*, the introduction of bromine (Kottenhahn, *Annalen*, 1891, **264**, 170; Kunkel, *Ber.*, 1904, **37**, 3485), the direct nitration of benzophenone and of the isomeric mononitrobenzophenones (Staedel, *Annalen*, 1878, **194**, 347; 1883, **218**, 344; 1895, **283**, 164), and the introduction of a nitro-group into certain 4-halogenobenzophenones (Montagne, *Ber.*, 1916, **49**, 2262), and it was found that the first substituent entered the unsubstituted nucleus, usually with the production of the three possible isomerides.

The nitration of 4-methylbenzophenone gave derivatives the structure of which seems to be uncertain (Zincke, *Ber.*, 1872, **5**, 685; 1874, **7**, 983; Limpricht, *Annalen*, 1895, **286**, 324).

These results and those observed in the diphenyl series show marked similarities, and it therefore seemed of interest to consider the substitution products of 4-hydroxybenzophenone and of its methyl ether.

The direct chlorination of 4-hydroxybenzophenone in acetic acid solution gave 3 : 5-*dichloro*-4-*hydroxybenzophenone*; under all the conditions tried, the same product was obtained.

The reaction of 4-hydroxybenzophenone with bromine could be regulated, and 3-bromo- and 3 : 5-dibromo-4-hydroxybenzophenone were obtained when the ketone, dissolved in acetic acid, was treated with the appropriate quantity of bromine. The same dibromo-derivative was obtained when the ketone was shaken with an aqueous bromine solution or treated in alkaline solution with bromine.

The iodination of 4-hydroxybenzophenone in alkaline solution yielded the 3-*iodo*-derivative; treatment with iodine monochloride in acetic acid solution gave 3 : 5-*di-iodo*-4-*hydroxybenzophenone*.

A single nitro-group was introduced into 4-hydroxybenzophenone by treating the ketone with nitric acid in glacial acetic acid solution at 50° or by merely dissolving it in cold nitric acid. Solution in nitric acid at 40° gave 3 : 5-dinitro-4-hydroxybenzophenone. Attempts to obtain higher substitution products seemed to result in partial oxidation.

The direct chlorination of the methyl ether could be controlled and 3-*chloro*- and 3 : 5-*dichloro*-4-*methoxybenzophenone* were isolated.

On bromination of the methyl ether, 3-*bromo*-4-*methoxybenzo*-

phenone was obtained under all conditions which did not involve a demethylation. In contrast to this, the chlorination of the monobromo-derivative proceeded smoothly and 3-*chloro*-5-*bromo*-4-*methoxybenzophenone* was obtained.

The introduction of one atom of iodine was effected with iodine monochloride, and higher iodination products than 3-iodo-4-methoxybenzophenone could not be obtained.

The formation of 3-*nitro*-4-*methoxybenzophenone* took place when the methoxybenzophenone was dissolved in fuming nitric acid. Nitration in a mixture of sulphuric and acetic acids yielded a mixture of dinitro-compounds; the formation of 3 : 3′-*dinitro*-4-*methoxybenzophenone* has been definitely established. A second isomeride is most probably 2′ : 3-dinitro-4-methoxybenzophenone, but this structure is based on a process of elimination of probable products. In addition to these isomerides there was a residue which after repeated crystallisations still seemed to be a mixture.

Trinitration products were obtained when nitration was effected in concentrated sulphuric acid solution. The formation of 3 : 3′ : 5 *trinitro*-4-*methoxybenzophenone* has been definitely established; an isomeride is shown to have two nitro-groups in the 3 : 5-positions and it is suggested that the third nitro-group is in the 2′-position. After the separation of the two pure products, a residue was obtained which could not be further purified.

The most suitable methods for the determination of the structure of the substitution products were : (*a*) oximation and conversion of the oximes into anilides. This procedure was found satisfactory provided not more than one nitro-group was present in the molecule; considerable difficulty was experienced in effecting the oximation of dinitro-derivatives, and the product could not be purified easily. (*b*) Synthesis of the substituted ketone by the Friedel–Crafts reaction was effective in the case of certain of the nitro-derivatives.

Oxidation to a substituted benzoic acid was not very satisfactory, as it was difficult to avoid complete oxidation of the molecule.

A survey of the results obtained shows that in 4-hydroxybenzophenone each ortho-position with respect to the hydroxyl group may be substituted with ease, irrespective of the nature of the substituting groups. Substitution in the opposite nucleus could not be effected before the 3 : 5-positions were filled.

The methyl ether behaves somewhat differently, in that one position only in the ortho-relationship to the methoxyl group is usually substituted. Chlorine behaves abnormally, in that both positions may be substituted by this reagent. On nitration, a second substituent enters the unsubstituted nucleus.

A comparison of these results with those obtained in the diphenyl

series shows that in each case the presence of a hydroxyl group promotes substitution in all vacant positions in the ortho-para relationship to this group; the presence of such groups as the halogens or the nitro-group inhibits substitution in the same nucleus.

The conversion of the hydroxyl group into the methoxyl group reduces the directive power, and although the first substituent enters in an ortho-position to this group, the second entering group usually goes into the opposite nucleus.

Experimental.

4-Methoxybenzophenone was prepared from anisole and benzoyl chloride by Gattermann's method (*Ber.*, 1890, **23**, 1204).

4-Hydroxybenzophenone.—The hydrolysis of all the methyl ethers was effected as follows: 5 G. of the ether and 20 c.c. of 48% hydrobromic acid were dissolved in acetic acid and refluxed for about 12 hours. Part of the acetic acid was then removed, and the residue poured into water. The acid was neutralised with ammonia, the product taken up in ether, and the hydroxy-ketone shaken out with a 10% solution of sodium hydroxide and reprecipitated with sulphuric acid. 4-Hydroxybenzophenone separated from dilute methyl alcohol in prisms, m. p. 135°.

4-Acetoxybenzophenone was prepared by acetylation in pyridine solution. It crystallised from dilute methyl alcohol in needles, m. p. 81° (Found: C, 74·8; H, 5·1. Calc. for $C_{15}H_{12}O_3$: C, 75·0; H, 5·0%).

3-Chloro-4-methoxybenzophenone was obtained when 4-methoxybenzophenone was treated with chlorine (slightly less than 1 mol.) in a cold solution of acetic acid. It separated from methyl alcohol in prisms, m. p. 98° (Found: Cl, 14·5. $C_{14}H_{11}O_2Cl$ requires Cl, 14·4%). On further chlorination in acetic acid solution, 3 : 5-dichloro-4-methoxybenzophenone (m. p. 74°) was obtained. The mono-derivative must therefore have been substituted in the 3-position.

3 : 5-Dichloro-4-methoxybenzophenone.—Into a solution of 10 g. of 4-methoxybenzophenone and 10 g. of fused sodium acetate in glacial acetic acid chlorine was passed until the gain in weight was 7 g. After some hours, the solution was poured into water. The product crystallised from alcohol in colourless needles, m. p. 74°. The same product was obtained by chlorination of the molten ketone in the presence of iodine or by chlorination in boiling carbon tetrachloride solution (Found: Cl, 25·2. $C_{14}H_{10}O_2Cl_2$ requires Cl, 25·3%).

The *α-oxime* was prepared by adding 10 g. of potassium hydroxide and 4·5 g. of hydroxylamine hydrochloride, each dissolved in the minimum quantity of water, to 6 g. of the dichloro-ketone dissolved in 100 c.c. of alcohol. The mixture was refluxed for 6 hours, the

alcohol in part removed, and the residue poured into water and neutralised with dilute hydrochloric acid. The oxime separated from alcohol in needles, m. p. 146° (Found : Cl, 23·9. $C_{14}H_{11}O_2NCl_2$ requires Cl, 24·0%).

3 : 5-*Dichloro*-4-*methoxybenzanilide*.—4 G. of the oxime, in dry ethereal solution, were treated with 7·5 g. of phosphorus pentachloride. After 12 hours, water was cautiously added and the ethereal layer was separated, washed, and dried. The *anilide*, after removal of the ether, crystallised from alcohol in pale yellow needles, m. p. 154° (Found : Cl, 23·95. $C_{14}H_{11}O_2NCl_2$ requires Cl, 24·0%).

On hydrolysis of the anilide (5 g.) with 20 c.c. of 10% hydrochloric acid for 6 hours at 140°, aniline and 3 : 5-*dichloroanisic acid* were obtained. 3 : 5-Dichloroanisic acid, prepared by the direct chlorination of anisic acid, crystallised from alcohol; m. p. 202° (Found : Cl, 32·05. $C_8H_6O_3Cl_2$ requires Cl, 32·1%). The acid was converted into the acid chloride, and the crude product added to a pyridine solution of aniline. The anilide thus obtained had m. p. 154°, alone or mixed with that prepared from the oxime.

3 : 5-*Dichloro*-4-*hydroxybenzophenone* was obtained from the methyl ether or by passing 5 g. of chlorine into a solution of 5 g. of 4-hydroxybenzophenone and 10 g. of sodium acetate in 100 c.c. of acetic acid and keeping the mixture for some hours. The product crystallised from methyl alcohol in needles, m. p. 148° (Found : Cl, 26·6. $C_{13}H_8O_2Cl_2$ requires Cl, 26·6%).

3-*Bromo*-4-*methoxybenzophenone*.—A solution of 5 g. of 4-methoxybenzophenone and 5 g. of sodium acetate in acetic acid was heated with 4·5 g. of bromine at 100° for 6 hours. The product separated from alcohol in needles, m. p. 94°. The same product was formed by bromination in the cold, in bright sunlight, or by heating together an intimate mixture of 5 g. of the ketone, 5 g. of sodium acetate, 4 g. of bromine, and 0·5 g. of pyridine (Found : Br, 27·5. $C_{14}H_{11}O_2Br$ requires Br, 27·5%).

Oximation of the ketone was carried out in the manner previously described. The *α-oxime* crystallised from alcohol in plates, m. p. 164° (Found : Br, 26·0. $C_{14}H_{12}O_2NBr$ requires Br, 26·15%). It was transformed into 3-*bromo*-4-*methoxybenzanilide*, which separated from alcohol in needles, m. p. 170° (Found : Br, 26·15. $C_{14}H_{12}O_2NBr$ requires Br, 26·15%). This anilide on hydrolysis yielded aniline and 3-bromoanisic acid and was prepared from the amine and the acid chloride.

The *β-oxime*, which remained in the mother-liquor, was precipitated with water. It separated from 30% aqueous alcohol in needles, m. p. 111·5° (Found : Br, 26·1. $C_{14}H_{12}O_2NBr$ requires Br, 26·15%). This oxime formed about 60% of the mixed oximes. On

transformation, *benzo-3-bromo-4-methoxyanilide* was obtained, which crystallised from alcohol in needles, m. p. 156° (Found : Br, 26·25. $C_{14}H_{12}O_2NBr$ requires Br, 26·15%). The anilide on hydrolysis gave 3-bromoanisidine (m. p. 56°) and was prepared from the amine and benzoyl chloride.

3-Bromo-4-hydroxybenzophenone was obtained by the hydrolysis of the methyl ether or by direct bromination of the ketone in acetic acid solution. It crystallised from alcohol in glistening needles, m. p. 183° (Found : Br, 28·75. Calc. for $C_{13}H_9O_2Br$: Br, 28·9%).

3-Chloro-5-bromo-4-methoxybenzophenone was obtained by leading chlorine into a glacial acetic acid solution of 5-bromo-4-methoxybenzophenone and fused sodium acetate, and precipitated after some hours by pouring the product into water. It separated from methyl alcohol in needles, m. p. 92° (Found : 0·1496 g. gave 0·1520 g. of silver halides. Calc.-weight, 0·1523 g.). The structure assigned depends upon the fact that in no case has chlorine been introduced into the unsubstituted ring.

3 : 5-Dibromo-4-hydroxybenzophenone resulted from (*a*) direct bromination of the ketone in acetic acid solution (compare Hantzsch, *Ber.*, 1906, **39**, 3094; Kostanecki, *Ber.*, 1907, **40**, 3662); (*b*) the addition of a 5% solution of bromine in potassium bromide to the ketone dissolved in an excess of dilute potassium hydroxide, the temperature being kept below 5°; and (*c*) by shaking the ketone with bromine water. The product separated from alcohol in needles, m. p. 155°.

The same product was obtained when an intimate mixture of fused sodium acetate and 4-methoxybenzophenone was treated with bromine in a sealed tube at 140°.

3-Iodo-4-methoxybenzophenone.—10 G. of 4-methoxybenzophenone, dissolved in 100 c.c. of acetic acid, were treated with 12 g. of iodine monochloride. After 2 days, the mixture was poured into water, and the colour discharged with sulphur dioxide. The semi-solid mass crystallised from alcohol in needles, m. p. 81° (Found : I, 37·3. $C_{14}H_{11}O_2I$ requires I, 37·6%).

The *α-oxime* crystallised from alcohol in needles, m. p. 182° (Found : I, 35·9. $C_{14}H_{12}O_2NI$ requires I, 36·0%). On conversion of this oxime, *3-iodo-4-methoxybenzanilide* was obtained, which separated from alcohol in faintly yellow needles, m. p. 206° (Found : I, 35·9. $C_{14}H_{12}O_2NI$ requires I, 36·0%). The anilide on hydrolysis yielded aniline and 3-iodoanisic acid. The acid separated from alcohol in needles, m. p. 240° (Found : I, 45·55. Calc. for $C_8H_7O_3I$: I, 45·65%). A specimen of the acid was prepared from *p*-cresol for comparison.

The β-*oxime*, precipitated from the mother-liquor on addition of water, crystallised from 30% alcohol in needles, m. p. 135° (Found: I, 35·8%). This oxime, on conversion, yielded *benz*-3-*iodo*-4-*methoxyanilide*, which crystallised from alcohol in needles, m. p. 164° (Found: I, 35·9. $C_{14}H_{12}O_2NI$ requires I, 36·0%). On hydrolysis, the anilide yielded 3-iodoanisidine, which separated from alcohol–light petroleum in needles, m. p. 75° (Found: I, 51·1. Calc. for C_7H_8ONI: I, 51·0%).

The anilide was prepared from *o*-anisidine by the following stages: *o*-anisidine was converted into *o*-iodoanisole and nitrated in glacial acetic acid solution. The 2-iodo-4-nitroanisole thus obtained was reduced to the amine, which was treated with benzoyl chloride in pyridine.

3-*Iodo*-4-*hydroxybenzophenone* was obtained on the hydrolysis of the methyl ether or by treating an alkaline solution of 4-hydroxybenzophenone with a 5% solution of iodine in potassium iodide. The product separated from methyl alcohol in plates, m. p. 184° (Found: I, 39·05. $C_{13}H_9O_2I$ requires I, 39·2%).

3 : 5-*Di-iodo*-4-*hydroxybenzophenone*.—5 G. of the hydroxyketone together with 10 g. of sodium acetate were dissolved in 100 c.c. of acetic acid and treated with 9 g. of iodine monochloride. After 12 hours, the mixture was poured into water; the precipitate obtained crystallised from alcohol in feathery needles, m. p. 145° (Found: I, 57·6. $C_{13}H_8O_2I_2$ requires I, 57·7%).

3-*Nitro*-4-*methoxybenzophenone*.—A solution of 5 g. of 4-methoxybenzophenone in 50 c.c. of nitric acid (*d* 1·5) was kept for 12 hours, and then poured on ice; the semi-solid product crystallised from alcohol in yellow needles, m. p. 105° (Found: N, 5·5. $C_{14}H_{11}O_4N$ requires N, 5·45%).

An oxime was obtained when 17 g. of the nitro-compound dissolved in alcohol were treated with 14 g. of hydroxylamine hydrochloride and 11·5 g. of potassium hydroxide, each dissolved in the minimum quantity of water. A red coloration appeared in the solution and acetic acid was added until the colour became yellowish-green. After refluxing for 3 hours, the oxime was extracted in the usual way. The α-*oxime*, after repeated crystallisations from alcohol, separated in yellow plates, m. p. 179° (Found: N, 10·3. $C_{14}H_{12}O_4N_2$ requires N, 10·3%). On conversion the oxime yielded 3-*nitro*-4-*methoxybenzanilide*, which separated from alcohol in needles, m. p. 163° (Found: N, 10·3. $C_{14}H_{12}O_4N_2$ requires N, 10·3%). This anilide on hydrolysis gave 3-nitroanisic acid and aniline, and was prepared from the amine and the acid chloride.

3-Nitro-4-hydroxybenzophenone was obtained when (*a*) the methyl ether was hydrolysed, (*b*) 5 g. of 4-hydroxybenzophenone,

dissolved in a mixture of 100 c.c. of acetic acid and 20 c.c. of acetic anhydride, were treated with 1·5 c.c. of nitric acid (*d* 1·5), dissolved in 10 c.c. of acetic acid at 50—60°, and (*c*) a solution of 5 g. of the hydroxy-ketone in 100 c.c. of nitric acid (*d* 1·4) was kept at 0° for 2 hours. The product crystallised from methyl alcohol in plates, m. p. 94° (Borsche, *Ber.*, 1917, **50**, 1339, gives m. p. 120—121°) (Found : N, 5·7. Calc. for $C_{13}H_9O_4N$: N, 5·75%).

3 : 5-*Dinitro*-4-*methoxybenzophenone*.—5 G. of 4-chloro-3 : 5-dinitrobenzophenone (Ullmann, *Annalen*, 1909, **366**, 92), dissolved in dry methyl alcohol, were treated with a solution of 1 g. of sodium in methyl alcohol. After 12 hours, the product was precipitated by pouring the mixture into dilute hydrochloric acid. It separated from methyl alcohol in yellow needles, m. p. 105° (Found : C, 55·5; H, 3·4. $C_{14}H_{10}O_6N_2$ requires C, 55·6; H, 3·3%).

3 : 5-Dinitro-4-hydroxybenzophenone was prepared by Ullmann's method (*loc. cit.*) or by heating a solution of 5 g. of 4-hydroxybenzophenone in 100 c.c. of nitric acid (*d* 1·4) at 40° for 30 minutes. It crystallised from alcohol in yellow needles, m. p. 138° (Found : N, 9·85. Calc. for $C_{13}H_8O_6N_2$: N, 9·75%). The product of direct nitration did not appear to be a single substance, but no other pure compound was isolated.

3′-*Nitro*-4-*methoxybenzophenone*.—18 G. of *m*-nitrobenzoyl chloride and 10·5 g. of anisole, dissolved in 100 c.c. of carbon disulphide, were treated with 25 g. of aluminium chloride at room temperature, and the reaction completed on the water-bath. The product crystallised from alcohol in faintly yellow needles, m. p. 95° (Found : N, 5·5. $C_{14}H_{11}O_4N$ requires N, 5·45%). On hydrolysis, 3′-nitro-4-hydroxybenzophenone was obtained.

3 : 3′-*Dinitro*-4-*methoxybenzophenone*.—(*a*) A solution of 5 g. of 3′-nitro-4-methoxybenzophenone in 50 c.c. of nitric acid (*d* 1·5) was kept over-night. (*b*) 15 G. of 4-methoxybenzophenone, dissolved in a mixture of 60 c.c. each of acetic and sulphuric acids, were treated with 10 c.c. of nitric acid (*d* 1·5) below 10°; the product, which was a mixture of isomerides, was crystallised from acetic acid and then repeatedly from alcohol until a pure substance was obtained. (*c*) 5 G. of 3-nitro-4-methoxybenzophenone were nitrated, in solution in a mixture of sulphuric and acetic acids, with 2 c.c. of nitric acid (*d* 1·5). The yield was about 70% of the mixed nitration product.

It separated from alcohol in faintly yellow needles, m. p. 143° (Found : N, 9·3. $C_{14}H_{10}O_6N_2$ requires N, 9·2%).

3 : 3′-*Dinitro*-4-*hydroxybenzophenone* was obtained on demethylation. It separated from alcohol in faintly green prisms, m. p. 165° (Found : N, 9·8. $C_{13}H_8O_6N_2$ requires N, 9·75%).

The structure of these compounds follows from their method of preparation.

3 : 4′-*Dinitro-4-methoxybenzophenone.* — 4′-Nitro-4-methoxybenzophenone (Auwers, *Ber.*, 1903, **36**, 3891) was nitrated by dissolving it in nitric acid (*d* 1·5) and keeping the solution for 12 hours. The product separated from alcohol in small prisms, m. p. 174° (Found : N, 9·3. $C_{14}H_{10}O_6N_2$ requires N, 9·3%).

3 : 3′ : 5-*Trinitro-4-methoxybenzophenone.*—(*a*) A solution of 10 g. of 4-methoxybenzophenone in a mixture of equal volumes of sulphuric acid and nitric acid (*d* 1·5) was kept for 2 days. The product was a mixture of isomerides, which were separated by successive crystallisations from acetic acid, toluene, and acetic acid. (*b*) 3 : 5-Dinitro-4-methoxybenzophenone was nitrated under the same conditions and the isomerides were separated. (*c*) 3 : 3′-Dinitro-4-methoxybenzophenone on nitration gave an almost quantitative yield of the trinitro-compound. This isomeride formed about 65% of the crude nitration product and was sparingly soluble in toluene; it separated from acetic acid in prisms, m. p. 184° (Found : N, 12·05. $C_{14}H_9O_8N_3$ requires N, 12·1%). The structure assigned is based on three observations : (1) on prolonged oxidation with chromic anhydride in acetic acid solution, a small quantity of *m*-nitrobenzoic acid (m. p. 140°) was isolated, (2) on further nitration the two dinitro-4-methoxybenzophenones both yielded the same product, and (3) 3 : 3′-dinitro-4-methoxybenzophenone yielded one trinitro-compound only.

2′(?) : 3-*Dinitro-4-methoxybenzophenone* was obtained when the 3 : 3′-dinitro-compound had all been removed from the crude nitration product. It was crystallised from toluene and then from acetic acid, separating in needles, m. p. 125° (Found : N, 9·35. $C_{14}H_{10}O_6N_2$ requires N, 9·3%).

2′(?) : 3 : 5-*Trinitro-4-methoxybenzophenone* was obtained from the crude nitration products of 4-methoxybenzophenone and of 3 : 5-dinitro-4-methoxybenzophenone. It crystallised from toluene in glistening, light yellow plates, m. p. 142° (Found : N, 12·1. $C_{14}H_9O_8N_3$ requires N, 12·1%).

A definite structure cannot be assigned to these compounds, as all attempts to prepare a pure specimen of 2′-nitro-4-methoxybenzophenone failed. Three out of the four most probable dinitro-4-methoxybenzophenones, however, have been obtained in a state of purity and the dinitro-4-methoxybenzophenone, m. p. 125°, was not identical with any of these compounds.

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CCCLXXXIV.—*The Temperature Effects of Mixing Non-aqueous Liquids.*

By WALTER MATTHEW MADGIN, JOHN BUTTERY PEEL, and HENRY VINCENT AIRD BRISCOE.

A GENERAL survey of the temperature changes occurring on mixing 628 pairs chosen from 37 non-aqueous liquids has shown that these changes are frequently of considerable magnitude (Madgin and Briscoe, *J. Soc. Chem. Ind.*, 1927, **46**, 107T). The present paper describes the further investigation of these changes in selected cases, undertaken in the expectation that some light might thereby be thrown upon the nature of liquids and liquid mixtures.

Relationship of Thermal Changes to the Polarity of the Constituent Liquids.—It has frequently been assumed (*e.g.*, Hildebrand, "Solubility," p. 85) that solubility is largely influenced by the relative polarity of the molecules concerned. The idea seems to be that a liquid composed of strongly polar molecules may easily dissolve another very polar liquid, but that the strong attraction between such polar molecules may hinder the interposition of non-polar molecules, and thus may even cause immiscibility with a non-polar liquid.

Detailed examination of the cases included in our original survey leads to the conclusion that there are many groups of liquids for which the relative values of the thermal effect of mixing differ widely from those to be expected from considerations of relative polarity. For example, hexane, benzene, and toluene are all very slightly polar by ordinary standards, and their polarities, as measured by the dielectric constant (*D.C.* = 1·85, 2·27, 2·34, respectively), increase slightly in the order named. In most cases the thermal effect of hexane with other liquids is more negative than that of benzene, which is again more negative than that of toluene. This is illustrated by the fact (Madgin and Briscoe, *loc. cit.*) that the number of positive heats of mixing given by hexane, benzene, and toluene, respectively, with the same set of other liquids is 0, 7, and 12. But in the case of the alcohols and carbon disulphide, benzene gives a greater decrease of temperature than either hexane or toluene; with alcohols, except methyl alcohol, toluene gives a greater negative effect than hexane; with methyl alcohol and carbon disulphide, hexane gives the greatest negative effect. These effects are not then in accordance with the order of dielectric constant.

Again, ethyl iodide generally gives a greater negative effect than ethyl bromide, which accords with the greater polarity of the former corresponding with the *D.C.* values: 9·4, 7·4; but exceptions

to this order occur in the heat effects with certain alcohols and carbon disulphide. Comparing the results of mixing ethylene dibromide, ethylene dichloride, chloroform, and bromoform with other liquids, it is noticeable that the chloro-compound generally gives the more positive heat of mixing, but exceptions occur in admixtures with ethyl and methyl iodides, with tetrachloroethane, and with aniline and carbon disulphide.

The doubt whether polarity can be assigned as a major cause of the temperature effects is intensified when we consider the cases in Table I and also that of water and ethyl alcohol (both having a

TABLE I.

	Dielectric constant.	Temperature change on mixing equal volumes.
Methyl acetate	7·1	− 5·1°
Ethyl iodide	7·4	
Ether	4·3	+ 14·2
Chloroform	5·1	
Acetone	21	+ 12·65
Chloroform	5·1	
Acetone	21	− 9·75
Carbon disulphide	2·6	
Acetone	21	− 6·95
Ethyl alcohol	25	

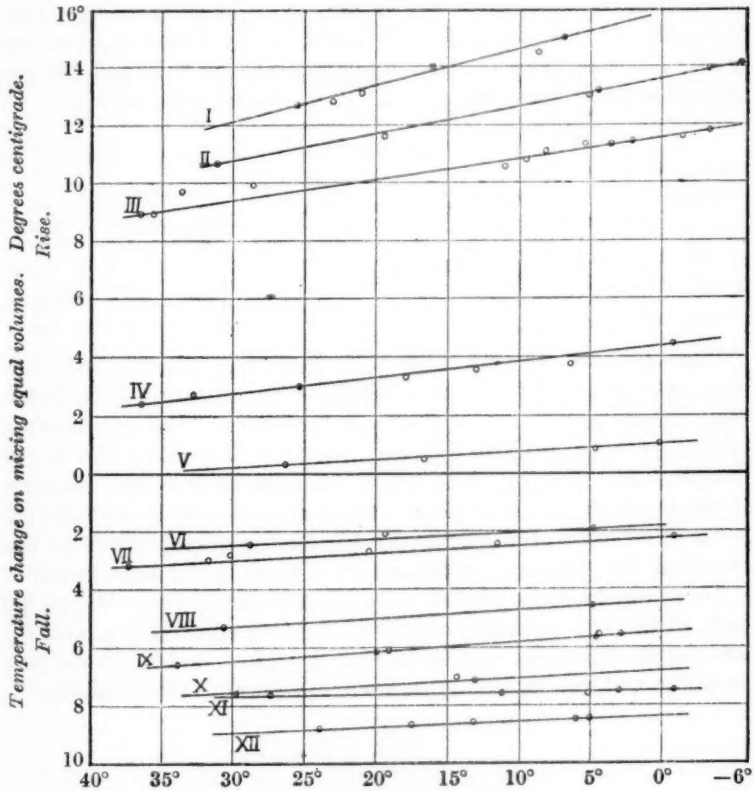
high *D.C.* and giving a rise of temperature on mixing), for it is apparent that either positive or negative heats of mixing may occur (*a*) with two liquids of small and similar *D.C.*, (*b*) with two liquids having respectively large and small *D.C.*'s, and (*c*) with two liquids both having large *D.C.*'s. Hence there seems to be no simple relationship between the heat of mixing and the polarity of the constituent molecules.

Effect of Variations of Initial Temperature on the Temperature Change on Mixing.—The literature contains very few references to investigations on the manner in which the temperature change on mixing varies with the initial temperature of the liquids mixed. Three isolated cases, two including water as one liquid, were investigated by Bussy and Buignet (*Ann. Chim. Phys.*, 1865, **4**, 5), and five cases, of which three included aniline as one liquid, have been investigated by Kremann and others (Kremann, *Monatsh.*, 1906, **27**, 91; Kremann and Pilch, *ibid.*, 1910, **31**, 203; Kremann, Meingast, and Guge, *ibid.*, 1914, **35**, 1235).

Therefore, as our general survey provided the necessary material for selection, it seemed well worth while to examine more widely the general trend of the thermal change with temperature for a series of mixtures ranging from those with large positive to those with large negative temperature changes on mixing. For this purpose, the apparatus used was a silvered Dewar tube (1″ diam. × 7″ deep

nternally) with narrow observation windows of the full height on opposite sides, provided near the mouth with three internal projections, on which rested the flange of a test-tube of such length that its thinly-blown closed end was about $\frac{1}{2}''$ from the bottom of the

FIG. 1.



Pairs of liquids.

I *o-Chlorophenol : aniline.* II *Chloroform : ether.* III *Chloroform : acetone.* IV *Chloroform : toluene.* V *Ether : toluene.* VI *Acetone : ether.* VII *Chloroform : hexane.* VIII *Ethyl alcohol : methyl acetate.* IX *Acetone : hexane.* X *Carbon disulphide : aniline.* XI *Carbon disulphide : ethyl oxalate.* XII *Carbon disulphide : acetone.*

Dewar tube. One liquid (10 c.c.) was placed in the Dewar tube, the other (10 c.c.) was within the test-tube : both were previously brought approximately to the desired temperature. In the test-tube were also a thermometer (− 20° to + 50° by 0·1°) and a pointed glass rod; when the tubes and liquids had attained the same constant temperature, the end of the test-tube was pierced by the

glass rod, the liquids were well mixed, and the temperature change was noted. To facilitate mixing, the denser of the two liquids was always put inside the test-tube. Twelve pairs of liquids were thus examined over a range of temperature; in most cases 6—8 observations were made, in some as many as 12. The whole of the observations are plotted in Fig. 1, and Table II gives for each pair of liquids (1) the temperature change from an initial temperature of 5°, (2) that from an initial temperature of 30°, and (3) the difference due to this change of 25° in the initial temperature.

TABLE II.

Pair of liquids.	1.	2.	3.	Pair of liquids.	1.	2.	3.
I	15·2	12·1	3·1	VII	−2·35	−3·0	0·65
II	13·1	10·8	2·3	VIII	−4·6	−5·3	0·7
III	11·15	9·4	1·75	IX	−5·65	−6·5	0·85
IV	4·1	2·8	1·3	X	−6·9	−7·6	0·7
V	0·9	0·2	0·7	XI	−7·6	−7·7	0·1
VI	−1·9	−2·4	0·5	XII	−8·5	−8·9	0·4

Inspection of the table shows at once that, whether the temperature change is positive or negative, its variation with initial temperature is always in the same direction; the temperature change is more positive (or less negative) the lower the initial temperature. On the other hand, the *magnitude* of the variation in temperature change obviously varies considerably throughout the series of mixtures, being generally greater the more positive (or less negative) the temperature change for a given initial temperature.

These observations receive a simple interpretation if, supposing each of the two liquids A and B to contain complex (A_x and B_y) and simple molecules, we assume that the latter, on admixture, may associate to form compound molecules, according to the scheme

$$\left.\begin{aligned} A_x &\rightleftharpoons xA \\ B_y &\rightleftharpoons yB \end{aligned}\right\} \rightleftharpoons zA_nB_m$$

and that the dissociations to the simple molecules are endothermic. The data here recorded are consistent with the view that alteration of the initial temperature changes the thermal effect in the A_nB_m equilibrium more than that in the A_x and B_y equilibria. This may occur through a change in the heat of reaction or through a shift of equilibrium, or for both of these reasons.

On entirely different grounds, Bramley (J., 1916, **109**, 43) reached a similar conclusion, which, therefore, whilst clearly needing further investigation, has a certain measure of probability.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research enabling the participation in

this work of one of us (J. B. P.), who has made a large number of the determinations of temperature change on which the present paper is based.

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CCCLXXXV.—*The Parachor and Chemical Constitution. Part VI. Some Cases of Supposed Ring-chain Tautomerism.*

By FREDERICK BASIL GARNER and SAMUEL SUGDEN.

THE strictly additive character of the parachor sets obvious limits to its application to problems of chemical constitution, for a change in position of a radical or of a linkage in the molecule has no effect upon the value of this constant. If, however, two isomeric substances differ in structure by the replacement of a double bond by a ring, they should exhibit differences in parachor which will be greater the greater the number of atoms in the ring. The conversion of a double bond into a four-membered ring should give a decrease in the parachor of 11·6 units, whilst the corresponding figures for five- and six-membered rings are 14·7 and 17·1, respectively (see values for ring constants, Sugden and Wilkins, this vol., p. 142).

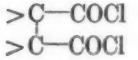
In this paper, the evidence of the parachor as to the structure of quinones, acid chlorides, and benzils is presented. Other substances in which similar structural changes have been postulated will be considered in later papers.

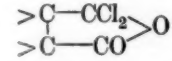
(1) *Quinones.*

Most of the reactions of *p*-quinones are represented by the formula (I), but the peroxide formula (II) has been suggested on chemical grounds by Graebe (*Annalen*, 1868, **146**, 1), whilst Hartley and Leonard (J., 1909, **95**, 34) and Haakh (*J. pr. Chem.*, 1910, **82**, 546), from a study of absorption spectra, and Binder (*Chem.-Ztg.*, 1921, **45**, 1114), from heats of combustion, also prefer formula (II).

(I.)

(II.)

(III.) 

(IV.) 

We have measured the parachors of *p*-benzoquinone and tolu-

quinone with the following results, from which it is evident that the liquid substances contain little or none of the peroxide form.

TABLE I.

	[P], obs.	[P], calc. (diketone).	[P], calc. (peroxide).
p-Benzoquinone.....	236·8	236·1	219·0
Toluquinone	272·0	275·1	258·0

(2) *Acid Chlorides.*

The chlorides of dibasic acids would normally be assigned formula (III); in some reactions, however, these substances behave as if they possessed the structure (IV).

Auger (*Ann. Chim.*, 1891, **22**, 36), on chemical evidence, considered that succinyl chloride was a mixture of the two forms, the unsymmetrical chloride being in large excess. This view was criticised by Morrell (J., 1914, **105**, 1733), who maintained that this substance should be represented by the symmetrical formula. Ott (*Annalen*, 1912, **392**, 245) agreed with this, although his determinations of molecular volume seemed to indicate the existence of an equilibrium mixture of the two forms.

Phthalyl chloride offers a still more interesting example, for it has been obtained in two isomeric modifications melting at 15° and 88·5° (Ott, *loc. cit.*; Scheiber, *Ber.*, 1913, **46**, 2368; Csányi, *Monatsh.*, 1919, **40**, 81). Ott (*loc. cit.*) and Pfeiffer (*Ber.*, 1922, **55**, 413) have shown that the less stable high-melting modification has probably the unsymmetrical formula, whilst the low-melting form has the symmetrical structure.

We have prepared and examined succinyl chloride and the two forms of phthalyl chloride, with the results shown in Table II.

TABLE II.

Substance.	[P], obs.	[P], calc. (symmetrical).	[P], calc. (unsymmetrical).
Succinyl chloride	282·6	282·6	267·9
Phthalyl chloride, m. p. 13° ...	373·9	377·5	362·8
Phthalyl chloride, m. p. 88·5°	367·8	377·5	362·8

For succinyl chloride, the parachor shows clearly that the liquid has the symmetrical formula and cannot contain an appreciable amount of the unsymmetrical modification. With phthalyl chloride, a difference in the expected direction is found between the two isomerides, but the parachors are not in very good agreement with the predicted value in either case. This is probably to be explained by interconversion of the isomerides (compare Csányi, *loc. cit.*); the high-melting form is rapidly changed to the low-melting form at temperatures above its m. p. and shows a pro-

gressive change of density when kept at 90° for an hour. The figure given for this substance therefore represents a mixture containing a little of the low-melting isomeride (see p. 2881). We were unable to prepare the low-melting form with a m. p. higher than 13° (Csányi gives 15°), and this may also have contained a little of the other isomeride. In general, therefore, the parachor confirms the conclusions of Ott and Pfeiffer as to the structure of the two forms of this substance.

(3) *Benzils.*

Benzil and its derivatives may be formulated either as diketones (V) or as peroxides (VI). From its reactions and colour, benzil itself is usually assumed to have the ketonic structure. Certain

(V.) $C_6H_5\cdot C(=O)\cdot C(=O)\cdot C_6H_5$ $\qquad$ $C_6H_5\cdot C(-O-)=C(-O-)\cdot C_6H_5$ (VI.)

alkyloxy-derivatives of benzil are white, or very pale yellow in colour (Irvine, J., 1907, **91**, 536), and the view has been expressed, notably by Schönberg and his collaborators (Schönberg and Kraemer, *Ber.*, 1922, **55**, 1174; Schönberg and Malchow, *ibid.*, p. 3746; Schönberg and Bleyberg, *ibid.*, p. 3753), that these derivatives should be represented by the peroxide formula (VI). It should be noted, however, that on fusion these substances give yellow liquids which are supposed by Schönberg to contain an equilibrium mixture of the two forms.

We have prepared and measured 2 : 2′-dimethoxybenzil (Irvine's white benzil) with the results shown in Table III. It will be seen that the parachors found are in good agreement with the values calculated for the diketone formula in both cases, and show no indication of the presence of even a small proportion of the isomeride having the peroxide structure.

TABLE III.

Substance.	[P], obs.	[P], calc. (diketone).	[P], calc. (peroxide).
Benzil	480·8	476·0	464·4
2 : 2′-Dimethoxybenzil	596·8	594·0	582·4

EXPERIMENTAL.

In the course of this work new measurements have been made of the surface tension and density of *p*-benzoquinone, toluquinone, succinyl chloride, phthalyl chloride, benzil, and 2 : 2′-dimethoxybenzil. Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). The constants for the bubbler used are: App. 14, $r_2 = 0{\cdot}177$ cm., $A = 0{\cdot}001020$. Densities were determined with the U-shaped pyknometer described previously (J., 1924, **125**,

1171), and are recorded in g. per c.c. All temperatures quoted are corrected by comparison with a standard thermometer with an N.P.L. certificate and are also corrected for exposed stem.

The tables are set out in the same manner as those given in earlier papers of this series and do not need further description. For all the substances studied in the present paper, d is very small and has been neglected.

p-*Benzoquinone*, $C_6H_4O_2$, $M = 108{\cdot}0$. A commercial specimen was purified by sublimation and melted at 115·5° (corr.). Some difficulty was encountered in the density determinations owing to the rapid sublimation of the substance into the cooler parts of the pyknometer; this sublimate was therefore removed and the tube reweighed after each volume determination. Densities determined: $D_{4^\circ}^{122^\circ}$ 1·085, $D_{4^\circ}^{132^\circ}$ 1·074, $D_{4^\circ}^{141{\cdot}5}$ 1·064, $D_{4^\circ}^{160{\cdot}5^\circ}$ 1·044, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}214 - 0{\cdot}00106t$.

t.	P.	D.	ϕ.*	γ.	Parachor.
123·5°	2989	1·083	1·0435	31·81	236·8
139·5	2800	1·066	1·0456	29·86	236·9
154·0	2613	1·051	1·0482	27·94	236·2
167·5	2518	1·036	1·0493	26·96	237·4
				Mean	236·8

* A correction factor; see J., 1924, **125**, 31.

Toluquinone (2-methyl-1 : 4-benzoquinone), $C_7H_6O_2$, $M = 122{\cdot}1$, was recrystallised from dilute alcohol and melted sharply at 67° (corr.). In the density measurements, errors due to sublimation were avoided by adopting the procedure described for benzoquinone. Densities determined: $D_{4^\circ}^{75{\cdot}5^\circ}$ 1·081, $D_{4^\circ}^{89{\cdot}5^\circ}$ 1·069, $D_{4^\circ}^{103{\cdot}5^\circ}$ 1·056, $D_{4^\circ}^{114{\cdot}5^\circ}$ 1·045, $D_{4^\circ}^{127{\cdot}5^\circ}$ 1·034, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}152 - 0{\cdot}000926t$.

t.	P.	D.	ϕ.	γ.	Parachor.
76·5°	3191	1·081	1·0406	33·86	272·3
92·5	3010	1·066	1·0424	32·00	272·4
107·5	2836	1·052	1·0444	30·21	272·0
121·0	2687	1·040	1·0464	28·67	271·7
131·0	2586	1·031	1·0478	27·63	271·6
				Mean	272·0

Succinyl chloride, $C_4H_4O_2Cl_2$, $M = 155{\cdot}0$, was prepared by the action of phosphorus pentachloride on succinic acid and purified by repeated distillation under diminished pressure and freezing. The final product melted at 18·5° (corr.) and boiled at 95° (corr.)/20 mm. Densities determined: $D_{4^\circ}^{21^\circ}$ 1·371, $D_{4^\circ}^{49^\circ}$ 1·339, $D_{4^\circ}^{66^\circ}$ 1·320, $D_{4^\circ}^{83{\cdot}5^\circ}$ 1·301, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}394 - 0{\cdot}00112t$.

t.	P.	D.	ϕ.	γ.	Parachor.
20·0°	3634	1·372	1·0452	38·75	281·8
49·5	3321	1·339	1·0483	35·50	282·5
65·0	3156	1·321	1·0502	33·81	283·0
79·5	2992	1·305	1·0522	32·21	282·9
				Mean	282·6

as-*Phthalyl chloride*, $C_8H_4O_2Cl_2$, $M = 203{\cdot}0$. Crude phthalyl chloride was prepared by the action of phosphorus pentachloride on phthalic anhydride and converted into the unsymmetrical form by heating with freshly prepared aluminium chloride (Ott, *loc. cit.*). The crude product was purified as described by Scheiber (*loc. cit.*) and Csányi (*loc. cit.*) by slow crystallisation from ligroin and mechanical separation of the prisms of the chloride from the needles of phthalic anhydride. After four crystallisations, a pure product was obtained, m. p. 88·5° (corr.).

This substance is transformed into the symmetrical modification at an appreciable rate even at temperatures just above the melting point. The stable form has a smaller density (1·327 at 90°), so that the transformation can be followed by the change in density. The following results were obtained when the pyknometer containing the unsymmetrical chloride was kept at 90° :

	First series.				Second series.			
Time (mins.) after melting	7	27	47	67	13	22	39	50
$D_{4°}^{90°}$	1·351	1·349	1·347	1·346	1·350	1·348	1·347	1·346

At the end of the experiment the substance was cooled rapidly and its m. p. found to be 81—83°, so that a considerable transformation had taken place. The crystals in the pyknometer (about 2 g.) required about 30 minutes in the bath at 90° to melt completely; it is evident, therefore, that the highest density found (1·351) is still a little lower than that of the pure substance at this temperature; the parachor will therefore be a little too large. The two isomerides have almost the same surface tension at 90°; hence no change in this constant with time was found for the unsymmetrical chloride.

t.	*P.*	*D.*	ϕ.	γ.	Parachor.
90°	3358	1·351	1·0482	35·88	367·8

s-*Phthalyl chloride*, $C_8H_4O_2Cl_2$, $M = 203{\cdot}0$. This substance is difficult to free from phthalic anhydride except by crystallisation from ligroin in a cold room (compare Csányi, *loc. cit.*). As such a room was not available, we converted the purified unsymmetrical form into the symmetrical modification by heating at 150° for 1 hour. The product was fractionated under diminished pressure and the specimen used had b. p. 150° (corr.)/23 mm. and m. p. 13° (corr.). (Csányi gives 15°, but we were unable to obtain a product with this melting point after repeated freezings.) Densities determined : $D_{4°}^{17·5°}$ 1·403, $D_{4°}^{26·5°}$ 1·381, $D_{4°}^{58°}$ 1·360, $D_{4°}^{68·5°}$ 1·349, $D_{4°}^{90°}$ 1·327, whence $D_{4°}^{t°} = 1{\cdot}420 - 0{\cdot}00104t$.

$t.$	$P.$	$D.$	$\phi.$	$\gamma.$	Parachor.
15°	4169	1·404	1·0403	44·23	372·9
40	3867	1·378	1·0427	41·12	373·0
61	3692	1·357	1·0440	39·31	374·5
90	3390	1·327	1·0469	36·20	375·3
					Mean 373·9

Benzil, $C_{14}H_{10}O_2$, $M = 210·1$, was recrystallised from alcohol and melted sharply at 95° (corr.). Densities determined: $D_{4°}^{102°}$ 1·084, $D_{4°}^{118·5°}$ 1·071, $D_{4°}^{134°}$ 1·059, $D_{4°}^{151°}$ 1·047, $D_{4°}^{163·5°}$ 1·037, whence $D_{4°}^{t°} = 1·161 - 0·00076t$.

$t.$	$P.$	$D.$	$\phi.$	$\gamma.$	Parachor.
103°	3573	1·083	1·0363	37·78	481·0
118·5	3415	1·071	1·0376	36·13	481·0
132	3289	1·061	1·0387	34·84	481·1
149	3125	1·048	1·0402	33·16	481·1
162	2984	1·039	1·0417	31·70	480·0
					Mean 480·8

2 : 2′-*Dimethoxybenzil*, $C_{16}H_{14}O_4$, $M = 270·2$. *o*-Methoxybenzaldehyde was first prepared by the careful methylation of salicylaldehyde with methyl sulphate: The aldehyde (1 mol.) and methyl sulphate (2 mols.) were mixed and mechanically stirred while caustic soda (5 mols.), dissolved in its own weight of water, was slowly added. The reaction vessel was well cooled and the addition of caustic soda stopped for a time when half of it had been added, the mixture having become a stiff cream; the addition of the remaining caustic soda caused the evolution of considerable heat, and the mixture became thinner. The stirring was continued for some hours after all the alkali had been added, and the mixture allowed to stand over-night. The crude product was separated, washed well with water, dissolved in ether, and the solution dried over calcium chloride. Finally, two distillations in a vacuum gave a pure product, b. p. 122°/20 mm., m. p. 37° (corr.).

The aldehyde was converted into the benzil, as described by Irvine (*loc. cit.*). The specimen used melted sharply at 130° (corr.). Densities determined: $D_{4°}^{130°}$ 1·128, $D_{4°}^{133°}$ 1·126, $D_{4°}^{146°}$ 1·116, $D_{4°}^{147·5°}$ 1·115, $D_{4°}^{163°}$ 1·104, $D_{4°}^{168·5°}$ 1·101, $D_{4°}^{187°}$ 1·086, whence $D_{4°}^{t°} = 1·217 - 0·00069t$.

$t.$	$P.$	$D.$	$\phi.$	$\gamma.$	Parachor.
137·5°	3557	1·122	1·0378	37·64	596·5
155·5	3419	1·110	1·0389	36·22	597·2
178	3207	1·094	1·0409	34·04	596·6
					Mean 596·8

Summary.

(1) Measurements have been made of the surface tension and density of quinone, toluquinone, succinyl chloride, the two forms of phthalyl chloride, benzil, and 2 : 2′-dimethoxybenzil.

(2) The parachors calculated from these observations indicate that, except in the case of phthalyl chloride, these substances have the normal structure, and in the liquid state cannot contain more than a small amount of the isomeride in which a new ring is formed by tautomeric change.

(3) The parachors of the phthalyl chlorides indicate that the lower-melting form has the symmetrical structure, whilst the higher-melting form has the unsymmetrical structure.

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CCCLXXXVI.—*The Chemical Nature of Precipitated Basic Cupric Carbonate.*

By JACK REGINALD IRONS HEPBURN.

THE author has previously studied (J., 1925, **127**, 1007) the mechanism of the changes which occur when precipitated cupric carbonate is kept in contact with the resulting solution. Special attention has now been directed towards the initial process which occurs on admixture of solutions of copper sulphate and sodium carbonate, the concentrations of which are systematically varied, with the object of gaining definite information as to the chemical nature of precipitated cupric carbonate, the composition of which is well known to depend on certain arbitrary factors, such as temperature of precipitation, relative proportions of admixed reagents, and time elapsing between precipitation and analysis. Serious analytical discrepancies have also been found to arise through inefficient mixing of the reacting solutions. In order to minimise such variations in the composition of the precipitate, a special mode of procedure was adopted in the present work.

If an excess of copper sulphate is used in the precipitation, and more especially if the sodium carbonate is added to the copper sulphate, the precipitate contains basic sulphate admixed with the basic carbonate. If the copper sulphate is added to excess of sodium carbonate, the precipitate consists of the basic carbonate, and the solution may contain carbonic acid, sodium hydrogen carbonate, or sodium carbonate, or mixtures of these compounds, according to the excess of sodium carbonate employed. On the other hand, with efficient stirring, and if the copper sulphate is

added to an equimolecular proportion of the sodium carbonate, the precipitate contains a relatively small percentage of basic sulphate, whilst the solution contains only carbonic acid and a small amount of dissolved copper.

The possibility of decomposition of the precipitate through subsequent drying or other further treatment was minimised by carrying out the analyses immediately after the reaction. The results thus obtained were reproducible, the effect of small temperature changes being unimportant.

In order to render the investigation as complete as possible, determinations have been made of copper and carbonic acid in the precipitate and in the solution after the reaction; of sodium carbonate remaining in solution, and adsorbed in the precipitate; and of adsorbed sulphate.

Experimental.

The solutions employed in the precipitations were all prepared by dilution from *M*-solutions. The cupric sulphate (A.R.) was used to standardise the sodium thiosulphate used in the subsequent copper estimations, and in the preparation of the *M*-cupric chloride solution. The cupric chloride employed was free from sulphate, but contained 22·9% of water; the solution was therefore made a little stronger than *M*, titrated against the standard thiosulphate solution, and diluted with the calculated amount of water. The *M*-sodium carbonate solution was standardised against the oxalic acid used in the carbon dioxide estimations, which had been previously standardised against pure sodium carbonate from bicarbonate. The oxalic acid was also employed in the estimations of sodium carbonate in solution. The potassium carbonate was prepared from bicarbonate and its titration against the oxalic acid confirmed the accuracy of the previous standardisation against sodium carbonate (Titration found: 27·65 c.c. Calc.: 27·67 c.c.). The barium hydroxide solution used in the estimations of carbon dioxide was preserved in an apparatus for titration in the absence of carbon dioxide. It was standardised against the oxalic acid.

The more dilute solutions were prepared in every case by dilution with water free from carbon dioxide and air. The volumes of the solutions employed were adjusted to yield a convenient quantity of precipitate, and varied from a minimum of 50 c.c. to a maximum of 1000 c.c. Equimolecular quantities of sodium carbonate and copper sulphate were used.

The experimental method adopted in the precipitations was similar to that described by Gröger (*Z. anorg. Chem.*, 1900, **24**, 127). The solution of copper sulphate was added in a fine stream

to that of sodium carbonate, violent mechanical stirring being employed throughout the addition. All the precipitations were carried out at room temperature (20°). The solution was filtered immediately after flocculation (5—10 minutes) through a Buchner funnel by means of the water-pump, and the precipitate was washed rapidly with cold water free from carbon dioxide and air.

Analysis.—(a) *Precipitate.* The moist precipitate was transferred to an apparatus for the estimation of carbon dioxide in carbonates (following the author's modification of Van Slyke's method, *Analyst*, 1926, **51**, 622), and analysed at once, loss of carbon dioxide from the precipitate through exposure to the air being thus eliminated. Copper was determined in the hydrochloric acid solution (remaining after the carbon dioxide estimation) by dilution, addition of sodium acetate in excess and of potassium iodide, and titration against standard sodium thiosulphate. Each determination was carried out in duplicate, except in Expts. 7 and 8 (Table I), where the amount of precipitate obtained was insufficient.

In the estimations of the adsorbed material in the precipitate, about 1 g. of the air-dried material was ignited to cupric oxide, extracted with boiling water, the filtrate concentrated, and titrated against 0·1*N*-oxalic acid for sodium carbonate (compare Applebey and Lane, J., 1918, **113**, 611). The remaining precipitate was dissolved in hydrochloric acid and added to the aqueous extract; the sulphate in the combined solution was then estimated as barium sulphate. (The solution was made up to 100 c.c. and 10 c.c. were titrated against the standard thiosulphate to determine the copper present, the remaining 90 c.c. being employed in the sulphate estimation.)

(b) *Filtrate.* A large volume of the filtrate was concentrated, whereby the copper was completely precipitated, with evolution of carbon dioxide; it was filtered off, dissolved in acetic acid, and titrated as usual. This filtrate was further concentrated and its sodium carbonate was estimated by titration in boiling solution against standard oxalic acid, phenolphthalein being used as indicator. Carbon dioxide in solution was determined by difference.

The results of the complete series of experiments (over a concentration range of M to 0·00625M) are given in Table I. The carbon dioxide content of the precipitate appears to vary continuously with the concentration of the reagents employed in the precipitation. The percentage of adsorbed copper sulphate at concentrations varying from 0·5M to 0·05M is small and erratic in nature; its variation is parallel to that in the concentration of the sodium carbonate remaining in solution (see Table V). The

TABLE I.

Expt. No.	Initial conc. (mols./litre).	Composition of precipitate. CO_2, g.	CuO, g.	Value of x in $2CuO,xCO_2$. x.	Mean.	Adsorbed $CuSO_4$, %.
1 a	1·00	0·1013	0·3480	1·052	1·044	—
b	,,	0·03704	0·1295	1·035		
2 a	0·50	0·09204	0·3146	1·058	1·052	0·16
b	,,	0·07145	0·2473	1·045		
3 a	0·25	0·05790	0·2200	0·952	0·945	1·84
b	,,	0·04290	0·1656	0·937		
4 a	0·10	0·0681	0·2845	0·906	0·902	2·25
b	,,	0·04508	0·1818	0·897		
5 a	0·05	0·02122	0·09572	0·802	0·798	2·21
b	,,	0·04296	0·1957	0·794		
6 a	0·025	0·03038	0·1476	0·744	0·737	—
b	,,	0·03833	0·1894	0·732		
7	0·0125	0·02004	0·1068	0·678	0·678	—
8	0·00625	0·02522	0·1463	0·623	0·623	—

percentage of adsorbed sodium carbonate is negligible. It seems probable that these small quantities of adsorbed material play no essential part in the reaction, and they have therefore been ignored in the following discussion.

The solubility of carbon dioxide in water at 20° corresponds with a concentration of 0·039M (Landolt–Börnstein, Tables, 5th Edn., 1923, 768). The solution resulting from admixture of approximately 0·25M-solutions of copper sulphate and sodium carbonate should therefore (from calculations based on the composition of the precipitate) be saturated with carbon dioxide; no effervescence occurred, however, on admixture of such solutions at 20°, whilst the effervescence was very slight in the case of 0·5M-solutions, and violent with M-solutions. The liquid in equilibrium with the precipitate from 0·5M-solutions appears, therefore, to be supersaturated with carbon dioxide, the concentration of carbon dioxide deduced from the composition of the precipitate being 0·119M. It was observed that the analytical figures for the precipitates from 0·5M-solutions and above were more variable than those for precipitates from more dilute solutions. This would be in accordance with the essential instability of supersaturated solutions and their sensitiveness towards small temperature changes. It will be noted particularly that the carbon dioxide content of the precipitates increases continuously until the concentration 0·5M is reached, but oscillates when this concentration is exceeded, suggesting a definite connexion between the concentrations of carbon dioxide in the liquid and the solid phases. It has accordingly been assumed that the concentration 0·119M for carbon dioxide in equilibrium with the precipitate was the maximum value possible.

All the experiments of Table I were carried out with copper sulphate and sodium carbonate. Precipitations with 0·5*M*- and 0·05*M*-cupric chloride and sodium carbonate, and with 0·5*M*- and 0·05*M*-copper sulphate and potassium carbonate, were also carried out, in order to ascertain whether the composition of the precipitated basic cupric carbonate was influenced to any extent by the acid and basic radicals associated with the cupric and carbonate ions (Table II). Although the results are not identical, and indicate some specific action of foreign ions, the composition of the precipitate approximates to the same value in each case.

TABLE II.

	Composition of precipitate.	
	Value of x in $2CuO,xCO_2$ for	
Precipitants used.	0·5*M*-Sols.	0·05*M*-Sols.
$CuSO_4$, Na_2CO_3	1·052	0·798
$CuCl_2$, Na_2CO_3	1·011	0·850
$CuSO_4$, K_2CO_3	0·999	0·833

Discussion.

The composition and the chemical nature of precipitated cupric carbonate have been investigated previously by several authors, and there is some divergency in the views expressed by them.

Gröger (*loc. cit.*) has studied the effect upon the carbon dioxide content of precipitated cupric carbonate, of steadily increasing the molecular proportion of sodium carbonate relative to copper sulphate. In his experiments, all the precipitations were carried out with *N*-solutions, and the concentration was not systematically varied as in the author's experiments, but the method of procedure was otherwise very similar. The products were air-dried before analysis. When the molecular ratio $Na_2CO_3 : CuSO_4$ was increased from 1·1 : 1 to 2 : 1, the carbon dioxide content was very much lowered (from $2CuO,1·012CO_2$ to $2CuO,0·802CO_2$). With a molecular ratio of 4 : 1 the carbon dioxide content was reduced still further ($2CuO,0·748CO_2$). The composition of the precipitate from approximately equimolecular quantities (1·1 : 1) of 0·5 *M*-solutions corresponds with $2CuO,1·012CO_2$, in close agreement with the author's result at this concentration, $2CuO,1·052CO_2$.

Employing sodium bicarbonate in place of the normal carbonate, Gröger found the carbon dioxide content of the precipitate to be increased—with approximately equimolecular solutions, the composition of the product corresponded with $2CuO,1·244CO_2$. He apparently regards the precipitated basic cupric carbonate as the decomposition product of the normal carbonate, for he states

(*loc. cit.*, p. 134) that it is not improbable that normal cupric carbonate is first formed and passes into the basic carbonate with loss of carbon dioxide. The high results for the carbon dioxide content of precipitates from sodium bicarbonate are held to agree with this view, by increasing the available carbon dioxide content of the reagent used, and so diminishing the extent of the decomposition. On the other hand, Gröger formulates the above product from bicarbonate as a definite compound, $8CuO,5CO_2,7H_2O$.

Pickering (J., 1909, 95, 1409) attempted to ascertain the composition of precipitated basic cupric carbonate by adding sodium carbonate to a solution of copper sulphate sufficiently weak to ensure the retention of any carbon dioxide liberated (0·05% of copper). He found that alkalinity was attained when 1·61 mols. of sodium carbonate had been added per mol. of copper sulphate, and thence deduced the formula $5CuO,2CO_2$ (or $2CuO,0{\cdot}80CO_2$) for the precipitated substance. Pickering apparently assumes that the composition of the precipitate is independent of the concentration employed in the precipitation. This assumption has already been shown by the author to be untenable. Further, since the sodium carbonate was added to the copper sulphate, Pickering's compound undoubtedly contained basic sulphate.

Dunnicliff and Lal (J., 1918, **113**, 718) claimed to have prepared two new basic carbonates by precipitation from cupric sulphate–sodium carbonate mixtures of stated concentration, under standard conditions. Their method consisted in the addition of a cold 10% solution of sodium carbonate to a half-saturated solution of copper sulphate. The precipitate was kept for 24 hours, washed free from sulphate, and dried at 96° to constant weight. The mean of a number of analyses led to the formula $13CuO,5CO_2,9H_2O$. The second compound, prepared by adding a mixture of 5% sodium carbonate and 5% sodium bicarbonate solutions to the copper sulphate solution, corresponded to the formula $7CuO,2CO_2,5H_2O$.

The underlying idea in the experiments of Dunnicliff and Lal appears to be that any substance of constant composition which can be prepared under standard conditions is a definite compound, but, as judged by the author's results, these so-called compounds probably form points in a continuous curve; further, they appear to have no well-marked individuality or characteristics which distinguish them from other precipitates as definite compounds.

Mond and Heberlein (J., 1919, **115**, 908) have determined the composition of basic cupric carbonate precipitated from approximately 0·05*M*-solutions, under different conditions. The results indicate, contrary to those of Gröger, that the composition of the precipitated basic cupric carbonate was constant and independent

of the molecular proportion of cupric sulphate and sodium carbonate, in mixtures containing amounts in the proportion of 1 : 1 and lower. The molecular ratio in the precipitate was $CuO : CO_2 = 2{\cdot}26 : 1$ (or $2CuO,0{\cdot}885CO_2$). The amount of adsorbed material was relatively large, as is to be expected in the absence of an efficient stirrer. They concluded that no well-defined compound of copper is obtained by precipitation, the composition altering according to the conditions.

From theoretical considerations, there are a number of possibilities as to the chemical nature of the precipitated basic cupric carbonate. The simplest (Pickering; Dunnicliff and Lal) is to assume that a definite compound, or series of compounds, is formed. This view appears to be untenable in the light of the present experiments. A second view (Gröger) regards the substances as a mixture of the normal carbonate and the hydrated oxide. The various products are then regarded as due to the partial decomposition of the normal carbonate, and the variations of composition observed are attributed to greater or less decomposition, under given experimental conditions. It follows from this view, by the application of the mass-action equation $[CuO][CO_2]/[CuCO_3] = K$, that the concentration of the carbon dioxide in solution (or of carbonic acid), after precipitation, should possess a constant value, independent of the concentrations of the initial solutions employed in the precipitations; for, since both the normal cupric carbonate and the hydrated oxide may be regarded as very sparingly soluble in water, their active masses in solution would be constant.

It follows further, from this argument, that the amount of carbon dioxide retained in the precipitate at any particular initial concentration will diminish as the concentration of the precipitating solution is diminished, in order that this limiting concentration of carbon dioxide may be attained, after which no further loss of carbon dioxide from the precipitate should take place. Further, it appears that at a certain limiting value, *i.e.*, an initial concentration which will yield a concentration of carbon dioxide in the mother-liquor just equal to the equilibrium value, the precipitate should consist of the hydrated oxide only, and be free from carbon dioxide.

The experimental results for the concentration of carbon dioxide in the mother-liquor indicate, however, that this concentration diminishes steadily with the initial concentration of the reagents employed; the experimental result is therefore directly opposed to that derived from a consideration of the theoretical basis of Gröger's idea. A similar result follows if the basic cupric carbonate is regarded as the product of hydrolysis of the normal carbonate.

Free (*J. Amer. Chem. Soc.*, 1908, **30**, 1366) has suggested that the precipitated basic cupric carbonates might be regarded as solid solutions of carbonic acid with hydrated cupric oxide. This view does not appear to be very probable.

Certain basic salts produced by precipitation have been subjected to phase-rule studies (compare Britton, J., 1925, **127**, 2796), and the results have been held to be comparable with those obtained in initial precipitation processes. It appears to be a condition of such studies—more particularly those employing Schreinemakers's method of residues—that the liquid phase should be in equilibrium with a definite solid phase (or phases), *i.e.*, a well-characterised (probably crystalline) substance. In cases where a definite product is not obtained (*e.g.*, a colloidal substance, as obtained by Carter and Hartshorne, J., 1923, **123**, 2223, in their study of the system ferric oxide–phosphoric acid) the phase-rule method yields no definite result. Further, sufficient time must be allowed in phase-rule studies to enable a definite equilibrium to be reached. When such a state has been attained, the solid phase in equilibrium with the liquid is generally found to be crystalline (compare Carter and Hartshorne, *loc. cit.*).

It appears, therefore, that the initial product in a precipitation change must be distinguished from that obtained in a phase-rule study, or, in the particular case under investigation, that the initial precipitate is entirely different in nature from the stable basic carbonate, malachite, which is obtained under special conditions (compare J., 1925, **127**, 1007).

For the particular conditions maintained in the author's experiments, the final products of the precipitation at each concentration (neglecting small amounts of fortuitous impurities) consisted of a solid phase containing cupric oxide and a liquid phase containing carbon dioxide together with sodium sulphate. When the concentration of carbon dioxide in solution is plotted against the carbon dioxide content of the precipitate, Curve I (Fig. 1), is obtained. The carbon dioxide content, a, of the solid phase is evidently a continuous function of that in the liquid phase, c; further there is an exponential relation between these two magnitudes. When the logarithms of the two quantities are plotted, the points obtained lie, within the limits of experimental error, along a straight line (Curve II; Fig. 1). These results, therefore, are in accordance with the criteria usually applied to adsorption effects.

According to Freundlich ("Colloid and Capillary Chemistry," 1926, p. 172), the general form of the adsorption isotherm is represented by the equation

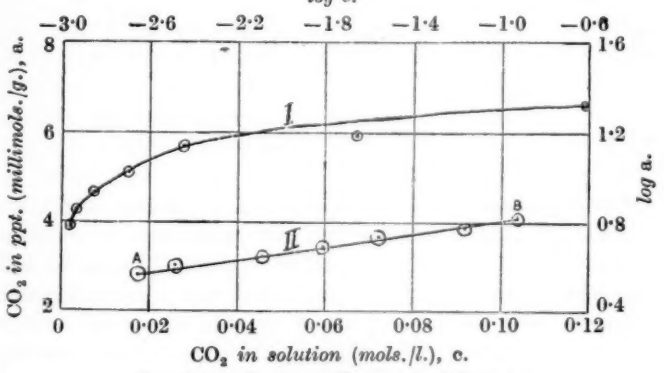
$$a = \propto (c)^{1/n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $1/n$ has a value between 0·1 and 0·5, whilst the constant α may vary within wide limits. [The concentration c is given in mols. per litre, whilst the quantity a is calculated in millimols. per g. of adsorbent (anhydrous cupric oxide).] The value of $1/n$ was calculated to be 0·130 from the co-ordinates of the points A and B, both of which fell on the logarithmic line. From this value and the observed values of a and c, α was found to be 8·75, by substitution in (1). Hence

$$a = 8{\cdot}75c^{0{\cdot}130} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

By use of this equation, the theoretical values for a have been calculated at the concentrations actually employed, and compared

FIG. 1.



For Curve I, use ordinary co-ordinates.
For Curve II, use logarithmic co-ordinates.

with the experimental figures (Table III, columns 2 and 3). The agreement appears to be satisfactory.

TABLE III.

Equil. conc. of CO_2 in soltn. (mols./l.).	CO_2 in precipitate (millimols. per g.). Found.	Calc.	Equil. conc. of CO_2 in soltn. (mols./l.).	CO_2 in precipitate (millimols. per g.). Found.	Calc.
0·119	6·61	(6·63)	0·00789	4·63	4·66
0·0668	5·94	6·15	0·00319	4·26	4·15
0·0275	5·67	5·48	0·00215	3·92	(3·94)
0·0150	5·01	5·07			

There is a marked parallelism between these results and those of Biltz (*Ber.*, 1904, **37**, 3138) for the adsorption of arsenious oxide by hydrated ferric oxide. Biltz's figures have been recalculated according to the adsorption equation

$$a = 6{\cdot}02c^{0{\cdot}200} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and the values obtained are in Table IV.

TABLE IV.

Equil. conc. of As_2O_3 in soltn. (mols./l.).	As_2O_3 in precipitate (millimols. per g.). Found.	Calc.	Equil. conc. of As_2O_3 in soltn. (mols./l.).	As_2O_3 in precipitate (millimols. per g.). Found.	Calc.
0·0979	3·77	(3·77)	0·0125	2·51	2·51
0·0603	3·40	3·43	0·00699	2·32	2·23
0·0479	3·26	3·28	0·00427	2·21	2·02
0·0422	3·10	3·19	0·00270	1·90	1·85
0·0330	2·99	3·04	0·00114	1·59	1·55
0·0240	2·82	2·85	0·00025	1·15	(1·15)
0·0178	2·75	2·69			

TABLE V.

Conc. of original solution (mols./litre).	Equil. conc. of CO_2 (mols./litre).	Conc. of Cu in solution (mols./litre).	% Cu not pptd.	Conc. of Na_2CO_3 in solution (mols./litre).	% Na_2CO_3 not pptd.
1·00	—	0·0047	0·94	0·0030	0·60
0·50	0·119	0·0049	1·98	0·0007	0·28
0·25	0·0668	0·0036	2·9	0·0014	1·1
0·10	0·0275	0·0018	3·6	0·0009	1·8
0·050	0·0150	0·0011	4·4	0·00034	1·4
0·025	0·0079	0·00071	5·6	0·00031	2·5
0·0125	0·0032	0·00050	8·0	Trace	—
0·00625	0·0022	0·00026	8·6	„	—

Further, the values for $1/n$ are within the limits laid down by Freundlich for typical adsorptions, but somewhat lower than the average (0·3—0·5), whilst the constant α is in both cases well within the range of values usual for such phenomena. A further parallelism appears in the nature of the adsorbed substance. The cases of adsorption from aqueous solution which have been investigated most thoroughly are those of the weak organic acids by charcoal, and in the present case the adsorbed substance is apparently carbonic acid, a weak acid the strength of which is of the same order of magnitude as those of the organic acids.

The precipitated cupric oxide appears to be present, when initially precipitated, in a very finely divided condition, as is indicated by the abnormally large solubility in the carbon dioxide in solution. Such a large effective surface would facilitate large and rapid adsorption.

The author therefore puts forward the view that the formation of precipitated cupric carbonate is due, not to dissociation of the normal carbonate, but to adsorption of un-ionised carbonic acid by hydrated cupric oxide in a very active state.

The fact that the composition of the basic cupric carbonate precipitated from 0·5*M*-solutions approximates to the formula $2CuO,CO_2$, independently of the particular salt of copper employed suggests that a definite compound is produced at this concentration. Further, this composition represents the maximum value for the

carbon dioxide content when the precipitations are carried out with sodium carbonate and copper sulphate. According to the views put forward by the author, however, the agreement of the analytical figures at this concentration with the formula for malachite is only a coincidence. The carbon dioxide content of the precipitate is conditioned by its concentration in the liquid phase, and the maximum value of this concentration is further limited by the solubility of carbon dioxide in water, which may, however, be affected by the formation of supersaturated solutions. If the solubility of carbon dioxide in water could be made to exceed this value, the carbon dioxide content of the precipitate would be expected to be higher. This prediction finds support in Gröger's results for precipitations with bicarbonate: in the presence of sodium bicarbonate the solubility of carbon dioxide is increased, and the concentration of un-ionised carbonic acid is further increased by the excess of bicarbonate ions, according to the relation $[H^{\cdot}][HCO_3']/[H_2CO_3] = K_1$. Actually, under these conditions the carbon dioxide content of the precipitate was increased.

The author has carried out a number of experiments with the object of approaching the equilibrium from the other side, *viz.*, from hydrated cupric oxide and aqueous solutions of carbon dioxide, but certain difficulties rendered it impossible to obtain definite results. Primarily, it was not found possible to prepare hydrated cupric oxide free from notable amounts of cupric sulphate, without the occurrence of blackening, due to traces of alkali. It is thought that more definite results might be obtained by the use of a more stable hydrogel, *e.g.*, hydrated ferric oxide.

The idea that certain basic salts might be adsorption compounds has recently been tentatively put forward by Britton (J., 1926, 125) to explain the fact that the thorium hydroxide precipitated from thorium nitrate by addition of potassium chromate contained large amounts of chromic anhydride, the presence of which was attributed to "a process akin to adsorption, in which the chemical tendencies of the weak acid and the weak base played an important part." Although no further experimental verification of this statement was adduced, the idea is analogous to that now suggested by the author.

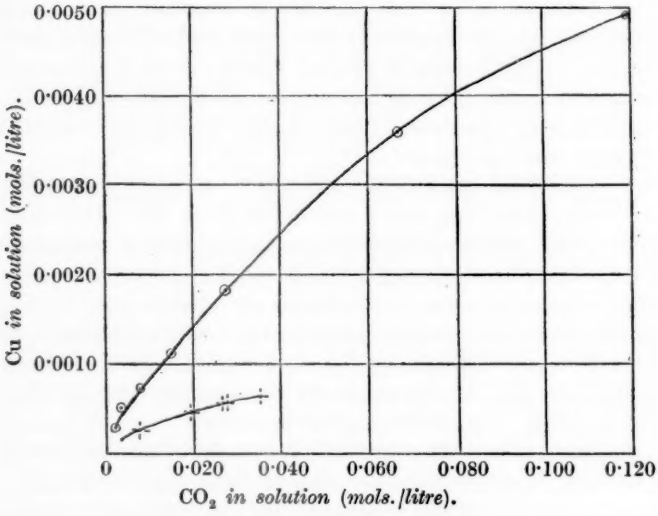
The Copper in Solution.

At every concentration at which the precipitation was carried out, it was found that a definite concentration of copper in solution was attained, after precipitation, dependent upon the concentration of carbon dioxide in the final solution. The relation between these two concentrations is represented by a smooth curve, shown in Fig. 2. The regularity of the results is striking, in view of the fact

that the carbon dioxide contents of the precipitates obtained at each concentration were widely divergent, the value of x in the formula $2CuO,xCO_2$ varying from 1·052 to 0·623; in spite of this, these precipitates behave in the same way as regards their solubility in aqueous solutions of carbon dioxide, which suggests that they are of very similar chemical nature. Such would be the case if each precipitate consisted of hydrated cupric oxide with variable quantities of adsorbed carbon dioxide.

Mond and Heberlein (*loc. cit.*) have determined the concentration of copper in the solution remaining after a precipitation from

FIG. 2.



⊙ *Author (see Table V).* ⊹ *Free.*

0·05*M*-solutions of cupric sulphate and sodium carbonate. They found this concentration to be 0·0032*M* (representing 8·0% of the total copper originally in solution), whereas the author's experiments at 0·05*M* gave 0·0011*M* (representing 4·42% of the original copper). Their corresponding concentrations of sodium carbonate remaining in the mother-liquor were also much higher than those found by the author. It is suggested that these high results are to be attributed to incomplete mixing owing to the lack of an efficient stirrer.

According to Mond and Heberlein, the dissolved copper is present in colloidal solution as the basic sulphate, and the sodium sulphate present in the solution may be removed by dialysis; they also state that the basic carbonate itself is not appreciably soluble in

water in the presence of carbon dioxide. In the author's opinion, these views are based upon insufficient experimental evidence, for the statement that the substance in solution is the basic sulphate appears to be founded upon one analysis of the precipitate formed after expelling carbon dioxide from the solution by boiling, whereby any carbon dioxide in the precipitate would also be removed. The black precipitate so produced contained $SO_3 : CuO = 1 : 4$.

The copper in solution is completely precipitated by boiling and expelling the carbon dioxide, the solution is colourless and not opalescent, and on exposure to air in an open vessel it loses carbon dioxide rapidly, with film formation of the basic carbonate on the surface. Under such conditions, it is difficult to understand how Mond and Heberlein were able to dialyse such a solution without decomposition and precipitation through loss of carbon dioxide.

Previous determinations of the solubility of basic cupric carbonate in aqueous solutions of carbon dioxide have been carried out by Free (*loc. cit.*). Precipitated basic cupric carbonate was agitated with a solution of carbon dioxide of known concentration, and the concentration of copper in solution was estimated after equilibrium had been attained. It was found that freshly precipitated basic cupric carbonate was more soluble in aqueous carbon dioxide solutions than the stable crystalline basic salt (malachite), and that the solubility of the freshly precipitated substance steadily decreased with time, finally reaching constancy at the value representing the solubility of malachite in the particular concentration of carbon dioxide. At the same time it was observed that the substance had been transformed into malachite.

The maximum value obtained by Free in any experiment was 107 parts of copper per million parts (or 0·00167 g.-atom per litre), in a solution of carbon dioxide containing 1200 parts per million. The author's result at this carbon dioxide concentration corresponds with 0·0018 g.-atom per litre. The agreement for freshly precipitated basic cupric carbonate is therefore satisfactory.

The author's results for the concentration of copper in solution are approximately three times as high as those obtained by Free for malachite (*e.g.*, for a solution containing 0·0275 mol. of CO_2 per litre, the concentration of Cu in solution was 0·0018 g.-atom per litre, whereas Free's result for a solution containing 0·0278 mol. of CO_2 per litre was 0·00054 g.-atom of Cu per litre). It is probable, therefore, that the freshly precipitated basic cupric carbonate is in a very finely divided condition, since below a certain limit of particle size the solubility of such precipitates is known to increase with the degree of dispersity. It may be observed, in this connexion, that Seyler (*Analyst*, 1908, **33**, 454) has attributed

the regularities found in Free's results to the formation of cupric bicarbonate in solution, and has attempted to show, by the application of ionic principles, that the solubility relationships are in accordance with this assumption.

Summary.

The effect of systematic variation in the concentration of the precipitants (copper sulphate and sodium carbonate) on the carbon dioxide content of precipitated basic cupric carbonate has been studied. The solutions employed were equimolecular, and the concentration ranged from M to $0{\cdot}00625M$. The results obtained indicate that the carbon dioxide content of the precipitate is a continuous function of the concentration of carbon dioxide in solution, and that these two magnitudes are capable of representation by a Freundlich adsorption equation. The view is therefore advanced that the formation of basic cupric carbonate is due to an adsorption process, the absorbent consisting of hydrated cupric oxide in a very active state, and the adsorbed material being un-ionised carbonic acid.

The author wishes to thank Dr. T. J. Drakeley for facilities provided during the course of this work.

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NOTES.

A Simple Form of Automatic Syphon. By DOUGLAS CREESE HARRISON.

THE syphon is made of glass tubing of diameter not greater than 5 mm. About eight capillaries of diameters varying between about ¼ mm. and 1 mm. and about 20 cm. long are drawn from the same tubing and placed inside the glass tube near one end. The tube is then heated not too strongly and bent to form the syphon, with the capillaries inside the bend and projecting about 7 cm. into the shorter limb of the syphon. The longer limb (which should extend well below the ends of the capillaries) is warmed and molten paraffin wax is drawn into it to within about 4 cm. of the ends of the capillaries. The wax is allowed to run down and the excess shaken out, so that, when cool, a thin, even layer remains on the inside of the tube. The wax serves to retain the drops of liquid drawn

FIG. 1.

through the capillaries by surface tension, until, within a few seconds, they have accumulated to form a column of liquid heavy enough to draw liquid over the bend of the large tube. The height to which the liquid can be raised in starting the syphon will depend, of course, on the surface tension of the liquid and the cross-section of the capillaries. It is advantageous to use a number of capillaries of various diameters, since the liquid will rise more rapidly and to a greater height in the smaller capillaries and, as the liquid begins to accumulate in the longer tube, the pull exerted by gravity will assist the syphoning of the liquid in the larger capillaries. In this way the flow will become faster and faster until the liquid is drawn over the bend and syphons in the large tube. The capillaries occupy only a small part of the tube and so allow a rapid flow of liquid through the syphon.—SHEFFIELD UNIVERSITY. [*Received, August 18th*, 1927.]

The Preparation of Triacetonamine Hydrate. By FRANCIS FRANCIS.

THE following method was devised some years ago, but was not described at the time, since it was desired to investigate the other products of the reaction and to increase materially the yield of the base.

Into a mixture of 2½ kg. of acetone and 800 g. of fused calcium chloride in a large round-bottom flask provided with an efficient condenser, ammonia is passed at intervals until the whole of the chloride has been converted into a liquid complex. After 3 days the product is gently boiled on a water-bath until the liquid calcium chloride–ammonia compound has decomposed and resolidified, ammonia being evolved. The dark, strongly smelling liquid is then decanted from the solid or pasty chloride, and distilled until a thermometer in the vapour registers 75°; the distillate consists chiefly of acetone. The residue is placed in a freezing mixture of ice and hydrochloric acid, and when the temperature has fallen to 1—2° an amount of water is added, with vigorous stirring, corresponding to a yield of 28% of triacetonamine calculated on the acetone used, *i.e.*, the amount taken less that distilled off. Triacetonamine hydrate separates in a crystalline condition as the temperature falls; after being pressed between filter-paper and recrystallised several times from undried ether, it is obtained in large, well-formed, slightly yellow crystals (yield, 20—26%, calculated on the acetone used).

The conversion of the hydrate into nitrosotriacetonamine is carried out in the usual manner and the yield is quantitative. The extreme ease with which this nitrosoamine is decomposed catalytic-

ally by alkalis, giving a nearly quantitative yield of phorone, renders this an elegant method for the preparation of this unsaturated ketone (J., 1912, **101**, 2358).—THE UNIVERSITY, BRISTOL. [*Received, September 15th*, 1927.]

7-Hydroxy-3-phenylcoumarin. By WILSON BAKER.

AN attempt was made to synthesise 3-phenylchromones (*iso*flavones; Baker and Robinson, J., 1925, **127**, 1981; 1926, 2713) by condensing ethyl α-formylphenylacetate with resorcinol or phloroglucinol in presence of phosphoric anhydride. By analogy with ethyl acetoacetate and its derivatives, chromones should be produced (see papers by Simonis and collaborators, *Ber.*, 1913, **46**, 2015; 1914, **47**, 692, 2229, etc.), but the first condensation gave only 7-hydroxy-3-phenylcoumarin, which has also been prepared (Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 121; Bargellini, *Gazzetta*, 1927, **57**, 459) from resorcylaldehyde, sodium phenylacetate, and acetic anhydride.

Jacobson and Ghosh (J., 1915, **107**, 1057) and Ghosh (J., 1916, **109**, 114) describe the reactions between ethyl α-formylphenylacetate and resorcinol, in presence of acetic acid and zinc chloride, and between formylphenylacetonitrile and resorcinol in presence of phosphoryl chloride, and the isolation in both cases of a substance, m. p. 131°, described by them as 7-hydroxy-3-phenylchromone. Since such condensations are now known to give coumarins (Baker and Robinson, J., 1925, **127**, 1981; Baker, *ibid.*, p. 2349; Bargellini, *Gazzetta*, 1925, **55**, 945), and the substance, m. p. 131°, could not be identical with 7-hydroxy-3-phenylcoumarin, which melts at 207—208°, the experiments were repeated, with the result that both gave the same product, m. p. 207—208°, identical in all respects with 7-hydroxy-3-phenylcoumarin. The product, m. p. 131°, is, therefore, not the product of these condensations, and its description is doubtless due to confusion of specimens in the laboratory.

7-Hydroxy-3-phenylcoumarin.—Ethyl α-formylphenylacetate (15 g.), xylene (75 c.c.), and resorcinol (50 g.) were heated at 160° for 2 hours, phosphoric anhydride (50 g.) being gradually added. The product, boiled with water to expel the xylene, was converted into the acetyl derivative, which, after twice recrystallising from acetic acid (charcoal), separated in colourless, flat prisms, m. p. 184—185°. No trace of an *iso*flavone could be detected in the mother-liquors. Hydrolysis produced 7-hydroxy-3-phenylcoumarin, which separated from alcohol in prisms, m. p. 207—208°, containing alcohol of crystallisation. The methyl ether, prepared by the action of methyl sulphate, crystallised from alcohol in colourless, nacreous plates, m. p. 124° (Bargellini, *loc. cit.*, gives m. p. 118—120°) (Found:

C, 76·0; H, 4·6. Calc.: C, 76·2; H, 4·8%). These compounds give yellow solutions in concentrated sulphuric acid, which exhibit an intense bluish-green fluorescence.

Condensation of Ethyl α-Formylphenylacetate with Phloroglucinol.—The two substances (15 g. of each), treated as previously described, gave an *acetyl* derivative (0·6 g.) which crystallised from acetic acid in hair-like, colourless needles, m. p. 255—256° (Found: C, 73·7, 73·6, 73·7; H, 4·2, 3·8, 4·6%; *M*, by Rast's method, 434, 416). Hydrolysis with potassium carbonate in 50% alcohol gave a phenolic substance which crystallised from alcohol in pale yellow prisms, m. p. 308—310° (decomp.) (Found: C, 72·2; H, 4·5%). This compound of high molecular weight is not identical with the 5 : 7-dihydroxy-3-phenylcoumarin prepared by Bargellini (*loc. cit.*). A number of empirical formulæ agree with the analyses, but without further experiments the selection of a definite formula is not possible. The phenolic *compound* gave with ferric chloride in alcoholic solution a yellow colour, and, like its acetyl derivative, dissolved in concentrated sulphuric acid to a bright yellow solution devoid of fluorescence.—The University, Manchester. [*Received*, *September* 13*th*, 1927.]

A Double Compound of Chromic and Hydrogen Chlorides. By James Riddick Partington and Sidney Keenlyside Tweedy.

If a concentrated solution of dark green chromic chloride is mixed with an equal volume of ether and slowly saturated with hydrogen chloride at 0°, the dark green chloride is precipitated. If the saturation is rapid, however, and the cooling bath is dispensed with, the solution becomes warm and besides dark green chromic chloride a heliotrope substance is precipitated. If the mixture is filtered with the aid of a pump, the green chloride often forms a layer of remarkably fine crystals on top of the heliotrope substance. The latter compound may be obtained in a fairly pure state if the stream of gas is stopped when the liquid is homogeneous and brownish-green, and after a while collects at the bottom of the vessel. The mother-liquor is decanted, the residue mixed with a large excess of ether, and after filtration the substance is air-dried. A further crop may be obtained by passing more hydrogen chloride into the mother-liquor, but after three such precipitations the product becomes largely contaminated with dark green chromic chloride. The substance may conveniently be washed with dry ether in a Soxhlet extractor (Found: Cr, 17·8, 17·3; Cl, 44·7, 44·9%. Constant values could not be obtained, showing that the product was never pure).

When freshly precipitated violet chromic chloride is washed with acetone in a Soxhlet extractor, if the acetone is warm when it falls upon the salt the surface of the latter becomes covered with a layer of the heliotrope substance, which in turn becomes covered with a layer of dark green chromic chloride. It would appear, then, that the heliotrope compound is also formed by the action of hydrogen chloride on the violet chloride when warm, since this acid is present in the freshly precipitated chloride.

The analyses agree roughly with the formula $CrCl_3,HCl,6H_2O$, which requires Cr, 17·2; Cl, 46·9%. Contamination with green or violet chromic chloride would cause the chromium content to increase and the chlorine content to decrease. No salts of this general formula have been described, but Larsson (*Z. anorg. Chem.*, 1920, **110**, 153) prepared two salts of composition $CrCl_3,MCl,5H_2O$, where M = Cs and Rb. A compound of this formula with M = H would require Cr, 18·2; Cl, 49·8%. The analyses will not fit in with any other type of double chloride formed by chromic chloride. Until the heliotrope substance can be prepared in a pure state, it can only be said that it is probably a double compound of the formula $CrCl_3,HCl,xH_2O$, where $x = 5$ or 6. The analyses and the method of preparation support the value $x = 6$.

Recoura (*Compt. rend.*, 1886, **102**, 922; *Ann. Chim. Phys.*, 1887, **10**, 49) records that when hydrogen chloride is passed into a chromic chloride solution for some days the latter turns brown and then red, and a soluble compound $CrCl_3,xHCl$ is formed, where x is greater than unity. On addition of ether, however, it is precipitated in unstable, green needles.

The heliotrope substance is insoluble in methyl and ethyl alcohols and dissolves in water to give a pink solution which immediately turns green, although of a different shade from that given by solutions of dark green chromic chloride. If a fragment of the substance is treated with a drop of water and observed under the microscope, it is seen that the process of solution is accompanied by very vigorous turbulence and agitation. It is not proposed at present to investigate the compound any further.—EAST LONDON COLLEGE, LONDON, E. 1. [*Received, October 6th*, 1927.]

The Viscosities of Chromic Anhydride Solutions. By JAMES RIDDICK PARTINGTON and SIDNEY KEENLYSIDE TWEEDY.

CHROMIC anhydride prepared and purified by the authors' method (J., 1926, 1142) had m. p. 193°. Melting points between 170° and 196° have been recorded in the literature. Both capillary-tube and test-tube methods were employed and the thermometer was com-